On the Recent Development of Quantum-Mechanical Solid-State Masers

Charles Chen-Hsi Tang, Ph. D.

Department of Physics

Abstract

A brief historical background and development of solid state Masers are presented first. A few relevent physical properties of paramagnentic substances are discussed and the basic principles and techniques of operation of both two-level and three-level Masers are reviewed. Finally a short discussion on the specific application and present status of the quantum-mechanical device is given.

INTRODUCTION

With the advance of the techniques of radio-frequency spectroscopy and the use of magnetic resonance method, as applied to molecular beams by Rabi etal (1938) and to nuclei of aggregated matter by Purcell, Torrey, and Pound (1946) and independently by Bloch, Hansen, and Packard (1946), the earliest observation related to the principles of the operation of a MASER (coined by C. H. Townes and his associates in 1955 from the words Microwave Amplification by Stimulated Emission of Radiation) was made by Purcell and Pound (1951) in a nuclear magnetic resonance experiment in connection with the concept of "negative temperature" in magnetism. This experiment demonstrated the stimulated radiation rather than absorption. The first use of magnetic resonance method was suggested in 1936 by Gorter in an attempt to detect nuclear magnetic spins by the nuclear resonance absorption of radio quanta through the heating of a crystal, but experimentally he was not

successful. Later, Rabi (1937) pointed out the use of the magnetic resonance method in atomic and molecular beams. The possibility of using both gas and solid substances to obtain microwave amplification utilizing coherent emission of radiation from systems at the stimulated energy levels was first discussed and presented by Weber (1953) and independently by Basov and Prokhovov (1954, 1955a). The first successful Maser (gas type) experiment was performed by Gordon, Zeiger, and Townes (1955) using the microwave spectroscopy technique and molecular beam separation method in obtaining ammonia molecular beams at an energy level higher than the "ground" level in order to obtain stimulated emission. Although the principles of the electron-spin two-level solid-state Maser was visualized earlier than those of the electron-spin three-level solid-state Maser, the latter was realized experimentally earlier than the former. The continuous pumping three-level solid-state Maser as proposed by Bloembergen (1956) had been operated successfully first by Scovil, Feher, and Seidel (1957) using isomorphous lanthanm ethyl sulfate as diluent doped with 0.5% gadolinium ethyl sulfate and 0.2% cerium ethyl sulfate. Later, McWhorter and Meyer (1958), Artman, Bloembergen and Shapiro (1958), Autler and Mcavoy (1958), and Kingston (1958) all used Potassium Cobalticyanide doped with 0.5% paramagnetic potassium chromicyanide as paramagnetic salt in their three-level Maser experiments with success. Ruby (Al_2o_3:Cr) was used also successfully in the operation of the three-level Maser by Makhov, Kihuchi, Lambe, and Terhune (1958). The first two-level solid state Maser of intermittant operation has recently been carried out by Chester, Wagner, and Castle (1958) using the technique of adiabatic fast passage. The materials they used were single crystals of quartz and of magnesium oxide irradiated by neutrons to introduce paramagnetic defects.

In microwave devices and electronic tubes, amplification results from the transformation or conversion of d-c power into microwave or signal power by the interaction of moving charged particles in electric or magnetic fields. In Maser devices amplification must be explained in

terms of the interatction of individual uncharged atoms or molecules with electromagnetic fields, and the internal energy of the atoms or molecules is directly transformed into microwave energy. Atoms and molecules can possess different amounts of internal energy determined by their electron or molecular configurations. The internal energy levels or configurations of the atoms and molecules are discrete or quantized. Atoms and molecules can be induced to gain or lose their quantized internal energy by the interaction with an electromagnetic field of proper frequency. When an ensemble of atoms or molecules are induced to give up their internal energy in a coherent fashion, amplification by stimulated emission of radiation results.

It is obvious that the development of the Maser was made possible by the recent advent of microwave and radio-frequency spectroscopy, and it is pertinent at this point to have an excursion to the field of spectroscopy in general. The varied applications of spectroscopy are well known, and the spectroscopic data accumulated in the infrared, visible, ultraviolet, X-ray, Gamma-ray, and Cosmic-ray regions are familiar. Important radio-frequency and microwave spectroscopy, however, emerges as a late comer since World War II. Generally speaking, spectroscopy in the visible and ultraviolet regions yields information on the energies of electrons in atoms and in molecules, whereas infrared spectrotroscopy furnishes information on the internal vibrations of the molecules themselves and on the overall rotations. By historical definition, X-rays are associated with rearrangements of atomic electrons involving deep-lying orbits and Bremstrahlung processes in X-ray tubes and Van de Graff machines, and they therefore also supply information of the atomic structure. Gamma-rays are often defined as electromagnetic radiation which appear during nuclear transitions following beta or alpha or nuclear reactions. Cosmic-rays were practically the only source of high energy particles available to physicists, until the recent development of electro-nuclear machines. With a certain range of overlapping, generally it can be said that molecular transitions occur in the infrared region, electronic transitions in the region from visible light

to X-rays, and nuclear transitions in Gamma-ray region. Microwave spectroscopy may be roughly defined as the study of interactions between matter and electromagnetic radiation at wavelengths ranging from about one millimeter to about one meter, although studies in the millimeter region still present difficulties at the present stage. A spectroscopic gap between the infrared and microwave region exists mainly because of the lack of known coherent sources and the low sensitivity of known heat detectors.

Historically, interest in microwave spectroscopy was initiated by the discovery of the absorption of microwave radiation in two gases: ammonia and water vapor. Cleeton and Williams (1934) published their observation on the absorption of microwave energy at 1.25 cm. in ammonia, and the absorption of microwave by oxygen and water vapor was discovered during World War II (Van Vleck 1947). The absorption in ammonia results from the "inversion" transition of the nitrogen atom in the ammonia molecule NH_3, whereas that in water vapor results from a rotational transition in water molecules. The gas Maser of Gordon, Zeiger, and Townes (1955) made use of the "inversion" transition of ammonia molecules. In such "molecular interaction" the microwave radiation is directly converted into the internal energy of molecules and vice versa. This is also a well-known process at very short wavelengths, for example, emission of incoherent visible light from a gas discharge. The advent of microwave spectroscopy realized the direct measurement of energy separations amounting to a fraction of wave number. These are intervals of just the order of magnitude needed in studying Zeeman and Stark splittings involved at low temperatures in adiabatic demagnetization, paramagnetic relaxation, etc.. By contrast, the decompositions involved in the nuclear magnetic resonance spectra are about a thousand times smaller and can be detected by radio-frequency rather than microwave spectroscopy. At the other extreme, Stark separations of several hundred wave numbers or more are of interest to the theory of magnetism at room temperatures and can sometimes be detected by infrared or visible spectroscopy, but the interpretation is often difficult because vibrational fine-structure can

easily be confused with that arising from the Stark effect.

The internal energies associated with nuclei, with electrons in atoms and molecules, with vibrations of atoms bound together in molecules and rotations of molecules themselves, and with the orientation of nuclear and electronic dipole moments in an applied electric or magnetic field, are all quantized, according to the quantum theory. These associated energies form a discrete set: that is, only those energy states leading to certain internal energies can exist. A single nucleus, electron, atom, or molecule can only exist in certain energy states determined by certain combinations of various quantum numbers (total quantum number, angular momentum quantum number, axial quantum number, and spin quantum number) or by the eigenvalues of the eigenvalue equation satisfied by the eigenfunctions of the energy. The emission or absorption of radiation by, say, a free atom takes place in accordance with resonance conditions which can be expressed in terms of quantum theory. A transition of the system from one of these discrete states to another, differing in energy from the first by ΔE, is accompanied by emission (or absorption) of radiation of the frequency $\nu=\frac{\Delta E}{h}$, where h is the Plank's constant. Consider, for the moment, a free electron in a magnetic field of strength H. Because of the intrinsic magnetic spin of the electron, this simple system will be found in one of the two possible states which differ in the orientation of the spin axis of the electron with respect to the magnetic field. The angular momentum $\bar{p}$ of any particle or system of particles is found to be easily expressed in terms of a multiple of a fundamental unit $\hbar$, which is Plank's constant divided by 2π, according to the rules of quantization of phase integral; and the magnetic moment $\bar{\mu}$ of an orbiting electron or a spinning spherical shell with charge e and mass m uniformly distributed over its surface is $\mu=\frac{-e}{2mc}\cdot\bar{p}$ It can be expressed as a multiple of a unit called "Bohr Magneton" μ_B and defined as $\frac{e\hbar}{2mc}$. The quantity usually denoted by S (electron spin, I for nuclear spin) is defined as $\frac{1}{\hbar}$ times the largest observable value of the time average of a component

of $\bar{p}$ in a given direction ($\bar{H}$ in this case), and the quantity which is truly a constant of motion is the square of the angular momentum with eigenvalues $S(S+1)\hbar^2$. For a particle of spin S there are $2S+1$ possible states or spin orientations and S can assume half-integer or integer values. For the present example of a free electron with $S=\frac{1}{2}$, the component of the angular momentum vector p in the direction of magnetic field H has either of the values $\hbar S=\frac{\hbar}{2}$ or $-\hbar S=-\frac{\hbar}{2}$. The energy of the Zeeman levels is given by the expression $E=-\mu\cdot\bar{H}=-\mu H\cos\theta$ The angle between the mangetic field vector and the mangetic moment vector is defined by the relation $\cos\theta=\frac{m}{S}$, where m is the magnetic quantum number running from $-S$ to S. Hence,

$$E=\frac{-\mu Hm}{S}=-g\frac{\mu B}{2}H,$$

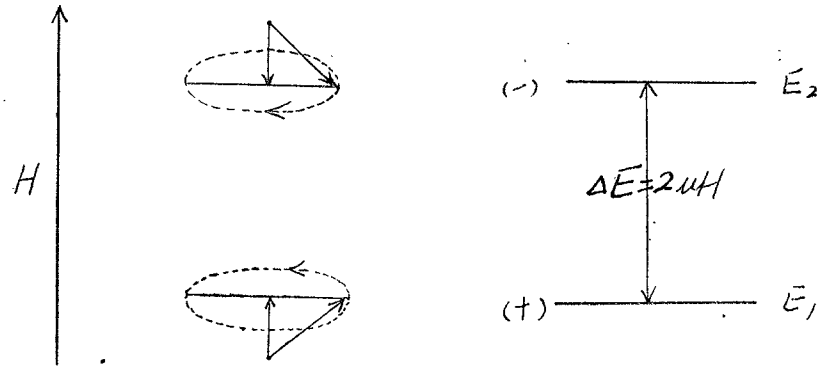
It is convenient to introduce here the g factor or spectroscopic splitting factor given by the Lande equation

$$g=1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

where S, L, and J denote respectively the spin, orbital, and total quantum number. The g factor is 2 in this example of a free magnetic spin. As shown in Figure 1 the two energy states of the free electron differ in energy by $2\mu H$, the work that would be required to reverse the direction of a magnet of strength which had originally been aligned with field H. This is derived from the fact that $\Delta E=-\mu H\Delta m/S$ and transitions are permitted only for $\Delta m=\pm 1$ according to the selection rules. The frequency of the transition is therefore

$$\nu=\frac{\mu H}{hS}=g\frac{\mu_B H}{h}$$

Consequently a measurement of field and frequency yields a value for the ratio of the electronic magnetic moment to the electronic spin.



The two energy states of an electron in a magnetic field H

Figure 1.

Let (−) denote the higher energy state in which the electronic spin is aligned against the magnetic field. The spin axis in most cases does not lie parallel to the direction of field H, but is tipped at an angle and precesses about the direction of the field in the way analogus to a tilted top. Only the components of spin and magnetic moment parallel to H are specified by S and μ. If the system is exposed to a radiation of proper frequency, a transition from one of the two states to the other should occur. A transition from (+) to (−) means absorption of a quantum of energy and that from (−) to (+) emission of a quantum. The former is called resonance absorption, whereas the latter stimulated emission. It is evident that what has been said in this section can be equally applied to an isolated nuclear spin I.

The magnetic properties of matter in aggregate can be divided generally into three parts, diamagnetism, paramagnetism, and ferromagnetism, which may include antiferromagnetism, and ferrimagnetism. They can be traced dominately to the electronic structure of the atoms of which the matter is composed; however, for many atoms the magnetic nature of atomic nuclei also contributes to the magnetism of matter. Although the magnetism that results from the nuclear properties is too weak to be observed under most circumstances in comparison with the electronic magnetism, techniques have been devised to observe

the nuclear magnetism. Since only paramagnetic substances are possibles Maser materials, paramagnetic properties of matter will be briefly presented in the following paragraphs.

Paramagnetism is mainly associated with nonvanishing electron spins in a system with feeble mutual interaction among the spins. It cocurs in all atoms and molecules having an odd number of electrons, all free atoms and ions with an unfilled inner shell, a few miscellaneous compounds with an even number of electrons, and in metals. Accordingly a substance is called paramagnetic if its atoms (or molecules) possess permanent magnetic moments with weak coupling among them.

Langevin's classical formula (1905) for the paramagnetic susceptibility is one of the most rudimentary applications of Boltzmann's statistics and is

$$X=\frac{M}{H}=\frac{N\mu^2}{3kT}=\frac{C}{T}$$

where the constant C is equal to $N\mu^2/3k$ and is called Curie constant. The $\frac{1}{T}$ temperature dependence is known as the Curie law. Langevin obtained the nonvanishing result only because of a subtle inconsistancy, since, if Boltzmann statistics were applied systematically to all degrees of freedom, the diamagnetic term and paramagnetic term cancel each other and no net magnetism would result. This was shown in 1911 by Niels Bohr and later by Miss van Leeuwan. The advent of quantum mechanics and electron spin threw sudden light to the calculation of magnetic susceptibilities. It turns out that Langevin's formula is still valid according to quantum mechanical calculation under certain stipulations. Because in electronically paramagnetic substances the spin and angular momentum are coupled to each other and to the crystalline electric field, ordinary spin-orbit multiplets and crystalline Stark splittings result. If the levels of the multiplet happen to be separated by an energy difference comparable to kT, a change in temperature will bring about a redistribution of the populations of the levels according to the Boltzmann factor $e^{-\frac{\mu H}{kT}}$ with an accompanying change in the effective magnetic moment. Curie's law fails in this situation. In order that

Langevin's formula for paramagnetic susceptibility may be valid, it is necessary that these multiplets or splittings have energy intervals which are either very large or very small compared with kT. On the other hand it is immaterial how the rotational and vibrational energy levels of the molecule are spaced relative to kT, since rigid rotations and small elastic vibrations do not appreciably affect the size of the resultant magnetic moment.

The study of paramagnetism reveals information about atomic and molecular structure. Paramagnetism is important in experimental physics because of the role it plays in low temperature physics, as the conventional method for attaining temperatures below 1°K utilizes the principle of adiabatic demagnetization of a paramagnetic salt. On the other hand, the extremely low temperature attained by adiabatic demagnetization helps to yield considerable information on small Stark splittings and coupling energies, and on relaxation behaviours at low temperatures. The first adiabatic demagnetization was performed in 1933, although theoretical discussion of the subject had been given a few years earlier by Debye and independently by Giauque. The basic idea is to cool a material by magnetizing it isothermally and demagnetizing it abiabadically a process in some way analogous to the cooling of a gas by isothermal compression and adiabaisc expansion. At a fixed temperature when a system of magnetic moments is subjected to a magnetic field, the moments will be partly ordered and the entropy of the system is accordingly lowered. On the other hand the entropy can also be lowered by lowering the temperature and the moments will line up more accordingly. If the magnetic field can be removed without changing the entropy of the system, the resulting rearrangment of the moments will resemble what it should be at a lower temperature.

The paramagnetic susceptibilities of metals do not follow Langevin's formula. They are only about a thousandth of what one would compute with this formula and are more or less independent of temperature. Pauli (1927) showed that the application of Fermi-Dirac statistics rather than Boltzmann statistics to the paramagnetic conduction electrons would

correct the theory of Langevin. The Fermi-Dirrac statistics can be regarded as a manifestation of the Pauli's exclusion principle.

What has been said so far in the above paragraphs is related to electronic magnetism. Since the important magnetic resonance method owes much to the study of nuclear magnetism, the techniques used in the study of electronic magnetism borrow heavily from those of nuclear magnetism. It is worthwhile to make a brief comparison between the nuclear magnetism and electronic magnetism in order to see more clearly the scope of magnetism in general and their applications in particular.

Electronic paramagnetism and nuclear paramagnetism are explained in exactly the same way, although in certain respects the nuclear paramagnetism is simpler due to the fact that electronic spin is inseparably bound up with the complicated atomic structure, whereas the nuclear ground state is separated from the excited nuclear states by an energy difference so large that the nucleus can be treated as almost isolated.

The nuclear static paramagnetic susceptibility of solid hydrogen, being diamagnetic with respect to electrons but paramagnetic with respect to protons, was first successfully measured by Lasarew and Schubnikow in 1937. Utilizing the $\frac{1}{T}$ temperature dependence in Curie's law, they cooled the hydrogen to 2°K where the nuclear Paramagnetism is no longer overshadowed by the electronic diamagnetism and made the measurement possible. The nuclear paramagnetism can be investigated much more easily by the magnetic resonance method of Purcell or Bloch (1946). The earliest experiment using magnetic resonance methods in investigating electronic paramagnetism was performed by Zavoisky (1945) at 10 cm. wavelength region. Other related methods of experimental study of the electronic paramagnetism had been performed earlier by Belz (1922) and Gorter (1936). Waller in 1932 first treated the interaction of spins with lattice vibration and laid the important foundation for the theory of electronic paramagnetism.

As mentioned in the preceding pages electronic paramagnetism

fails to follow Curie's law at temperature range T when μH is comparable to kT; however, nuclear paramagnetism does not deviate from the simple behaviors predicted by Curie's law. Generally speaking, the phenomenon of saturation becomes noticeable when μH and kT in the Boltzmann distributon $e^{-\frac{\mu H}{kT}}$ are comparable. Since nuclear magnetic moments are about one thousand times smaller than electronic magnetic moments, at reasonable magnetic field strengths electronic saturation phenomenon results at a few degrees Kelvin but nuclear saturation phenomenon at about one thousandth of a degree Kelvin. Hence, saturation plays no role in nuclear magnetism under ordinary conditions.

The local field of nuclear spin is very much weaker than that of electronic spin and it does not present complications in nuclear cases as it does in electronic cases. The "quenching" effect of internal electric fields on the electron orbits in a crystal is rather important in the study of electronic paramagnetism, but the electronic field gradients purturb only very, very slightly the nucleus which is tightly put together. Hence. the "quenching" effect of electronic type has no analogue in the study of nuclear paramagnetism. Although the effect of electron exchange force plays a decisive role in ferromagnetism, it only assumes a noticeable role in electronic paramagnetism in the form of "line narrowing" (Van Vleck 1957). On the other hand, exchange force has no role in nuclear paramagnetism, because the nuclear wave functions of two adjacent atoms practically do not overlap. The relaxation phenomena in electronic paramagnetism is considerably complicated by the interactions to which the electrons are subject, whereas rapid progress has been made in the understanding of nuclear spin relaxation phenomena. Thorough quantitative understanding of electronic relaxation phenomena is not in sight yet.

Every nucleus with spin greater than one half has a quadrupole moment. This is equivalent to, say, that the electric charge distribution of the nucleus is in general not spherical, e.g. ellipsoidal. If an ellipsoidal nucleus is subjected to an electric field gradient, it experiences a torque and precesses very much in the same way as the earth

experiences a torque and precesses in consequence of the elliplicity of the earth and the nonuniformity of the gravitational fields of the sun and moon. A nuclear electric quadrupole moment has the effect of splitting the magnetic resonance line. The effect of the nuclear electric quadrupole moment in nuclear magnetism has no counterpart in electronic magnetism.

Fundamentals

The operation of a Maser is described in terms of the interaction of individual atoms or molecules with electromagnetic fields; namely, the processes of stimulated emission and absorption. A simple general relationship between Einstein's A coefficient (spontaneous emission coefficient) and B coefficient (stimulated absorption or emission coefficient) is

$$B=\frac{\lambda^3}{8\pi h}A, \qquad (4)$$

Where λ is the resonant wavelength of the transition.

The actual theoretical evaluation of the spontaneous emission coefficient A in terms of quantum mechanical language depends upon the matrix elements between the wave functions of the two states involved in the transition. A brief description of the quantum theory of radiative transition is presented in the following paragraph.

Let ψ_n (x, y, z) be an eigenfunction of the energy. Then ψ_n will satisfy the eigenvalue equation

$$H\psi_n = E_n \psi_n \qquad (5)$$

where H is the Hamiltonian operator and E_n the eigenvalue of the eigenvalue equation. The time dependent eigenfunction

$$\psi_n(x, y, z, t)=\psi(x, y, z)e^{-i\frac{}{\hbar}t} \qquad (6)$$

will satisfy the Schroedinger time dependent equation

$$H\psi=E_n\psi_n=-\frac{\hbar}{i}\frac{\partial}{\partial t}\psi_n \qquad (7)$$

Hence ψ_n will remain a solution at subsequent times, and it also

continues to satisfy the eigenvalue equation (5) with the same eigenvalue, E_n. This essentially implies that the eigenfunctions of the energy in the form of equation (6) are independent of time and are consequently called stationary states. The probability density P (x,y,z,t) for such eigenstates of the energy is also independent of time since

$$P(x,y,z,t)=\psi_n^* \psi_n = \psi_n^* e^{i\frac{E_n}{\hbar}t} \psi_n e^{-i\frac{E_n}{\hbar}t} \qquad (8)$$
$$= |\psi_n(x,y,z)|^2$$

These properties are not true of eigenstates in general, but eigenstates of energy are unique because of the occurrence of the Hamiltonian in the Schroedinger's time dependent equation. One might be led to think at this point that according to the above derivation there should be no radiative transitions from one energy level to another because the energy levels are "stationary." However, this is not the case according to experience. The reason is that the Hamiltonian used above is not complete since it is only the Hamiltonian of an isolated atom. The picture is different under an actual situation, as it is evident that the atom is not isolated at all but instead is always in the presence of a radiation field either due to other atoms or an incident wave. Hence the complete Hamiltonian of the atom must include all these effects of interaction with the radiation field, and the energy states thus determined are no longer stationary states of the complete problem including interactions. With this in mind it is easy to see that transitions between the previously determined energy levels can take place and these transitions occur in the form of emission of radiation or absorption of radiation. It is the interradiation with the radiation field which makes the transition possible. For a detailed quantitative treatment of the subject the reader is referred to the book **Quantum Mechanics** by Dirac or **Quantum Theory of Radiation** by Heitler. However, the results obtained by the quantum mechanical calculation for the rate of radiation of energy by the dipole moment of the atom do not appear to be too complicated and have a simple correspondance with those obtained by the classical calculation. The classical electromagnetic theory shows that a charge e in simple harmonic motion of frequency

and amplitude $\bar{r}=r_0 \sin 2\pi\nu t$ radiates energy at the rate of W ergs per second where

$$W=\frac{2}{3}\frac{e^2}{C^3}\left|\ddot{\bar{r}}\right|^2=\frac{2}{3}\frac{e^2}{C^3}\left|(2\pi\nu)^2\bar{r}\right|^2=\frac{64\pi^4\nu^4}{3C^3}\left[\frac{1}{2}\left|e\bar{r}\right|^2\right] \quad (9)$$

The quantum mechanical calculation of the total intensity of radiation W_{m-n} emitted per second when the atom goes from state m to state n is just the same as the classical radiation intensity at this transition frequency, except that the quantity, $\frac{1}{2}\left|e\bar{r}\right|^2$, in the classical expression should be replaced by the modulus square of the so-called matrix element $(m\,|\,e\bar{r}\,|\,n)$ of er, where

$$|(m\,|\,e\bar{r}\,|\,n)|^2=\left|\int\psi_m^*\, e\bar{r}\,\psi_n\, d\tau\right|^2=|\mu|^2 \quad (10)$$

Accordingly the quantum mechanical expression for the rate of total intensity of radiation is

$$W_{m\ n}=\frac{64\pi^4\nu^4}{3C^3}\left|\int\psi_m^*\, er\,\psi_n\, d\tau\right|^2 \quad (11)$$

It is to be noticed that the above expression is only for the spontaneous emission of radiation by an atom in a higher state m to a lower state n. In other words equation (11) applies only to spontaneous radiation of an atom in a state above "ground" state and in the absence of any incident radiation. In the presence of an incident radiation of proper frequency ν, either induced emission or absorption will occur in addition to the spontaneous emission. If equation (11) is divided by the amount of energy in a photon, $h\nu$, then

$$\frac{64\, n^4\nu^3}{3h\, C^3}\left|\int\psi_m^*\, e\bar{r}\,\psi_n\, d\tau\right|^2$$

is the number of photons of energy radiated per second. This is exactly the meaning of Einstein's A coefficient which is the probability of spontanneous emission of a photon per second; that is,

$$A=\frac{64\pi^4}{3h\lambda^3}\left|\int\psi_m^*\, e\bar{r}\,\psi_n\, d\tau\right|^2 \quad (12)$$

In Maser devices equation (12) is important in estimating the noise due to spontaneous emission, and this source of radiation is the ultimate limitation to the noise figure of a Maser.

It follows from equation (4) that the induced transition coefficient B is

$$B=\frac{8\pi^3}{3h^2}\,|\int\psi_m^*\,e\bar{r}\,\psi_n\,d\tau\,|^2=\frac{2\pi}{3\hbar^2}\,|\,\mu\,|^2 \qquad (13)$$

which is interpreted as the probability of induced transition per unit incident spectral energy density. For the case of polarized incident radiation the probability of the induced transition is, for each atom,

$$p=\frac{8\pi^3}{h^2}\,|\int\psi_m^*\,e\bar{r}\,\psi_n\,d\tau\,|^2\,I=\frac{2\pi}{\hbar^2}\,|\,\mu\,|^2 I \qquad (14)$$

where I is the incident spectral energy density of a particular polarization. Suppose that the incident rf radiation has a bandwidth Δf. The energy density of the radiation field may be taken as $U = I\Delta f$. If the atomic bandwidth for the transitions is considerably greater than the incident bandwidth then a fraction $\Delta f/\Delta\nu$ of the atoms can be induced to make a transition, where $\Delta\nu$ is the atomic bandwidth.

The power absorption due to induced transitions depends upon the number of atoms available for transition. At this point, it will be convenient to label the number of atoms available as N_e for the effective number. N_e will nearly always be less than the total number of atoms in the system (crystal or beam). The power output is, then, N_e times the energy per atomic transition ($h\nu$) times the probability of a transition per second. That is, the power output P is given by

$$P=N_e\,h\nu.p \qquad (15)$$

This may be combined with equation (14) to give

$$P=\frac{8\pi^3 N_e\,\nu|\mu^2 U}{h\triangle\nu} \qquad (16)$$

This equation is useful for evaluating power absorbed (or emitted) at resonance.

A word is in order to show how this effective number N_e comes about. It has been mentioned above that the spectral emission or absorption of the atom can be achieved by shining proper radiation on it. Many elements in gaseous form, especially the vapours of metals, emit line spectra upon being heated. It is a familiar phenomenon that sodium vapour, when heated by a Bunsen flame, will emit the well-known D-lines. In such cases, it is evident that the atoms or molecules are excited by thermal agitation. A simple theoretical deduction

from statistical mechanics shows that when a substance is in thermal equilibrium, the average mumber or population N_i in a quantum state in which the atmic or molecular energy is E_i, is

$$N_i = Ce^{-\frac{E_i}{kT}} \tag{17}$$

Equation (17) is known as the Boltzmann distribution factor for the quantized system. Thus the number in the state goes down exponentially with an increase in the energy of the state. If state E_2 has greater energy than state E_1, the ratio of the number of atoms in the two states will be

$$\frac{N_2}{N} = e^{-\frac{E_2 - E_1}{kT}} = e^{-\frac{h\nu}{kT}} \tag{18}$$

In thermal equilibrium the number of systems in the lower energy state E_2 is in excess of that in the higher energy state E_2 by the effective number N_e.

$$N_e = N_1 - N_2 = N_1(1 - e^{-\frac{\nu}{kT}}) \doteq \frac{N}{2}\frac{h\nu}{kT} \tag{19}$$

for $h\nu \ll kT$. where $N = N_1 + N_2$ is the total number of the systems. In the microwave region the approximation $h\nu \ll kT$ always holds e.g., at $\nu = 10^{10}$ cycles and $T = 1°K$, kT is about one hundred times larger than $h\nu$. With N_e expressed as in equation (19) the power absorption (or emission with population reversed) of equation (16) becomes

$$P = \frac{4\pi N\nu^2|\mu|^2 U}{kT\triangle\nu} \tag{20}$$

From equation (20) one sees that the power output will increase with the frequency and inversely with the bandwidth of the collection of atoms. U, the energy density of the rf radiation is a linear term, but just as in the case of any other amplifier, there will be a saturation region. For sufficiently large values of U, the power absorption (or emission) will not increase and will, in fact, drop to zero because all the available transitions are canceled by emission (or absorption). This is explained by the fact that (1) the Einstein B coefficient is the same for both absorption and induced emission, (2)

the incident radiation tends to equalize the population of the two levels. If U becomes large, the value of N_e tends to zero. This effect of incident radiation on the level population is callad saturation (Karplus and Schwinger, 1948). In terms of equation (19) it can be said that saturation tends to increase the temperature T of the system and thereby reduce the number N_e.

It is seen from equations (12) and (13) that to evaluate both A-coefficient and B-coefficient is to evaluate the integral $\int \psi_m^* e\bar{r}\psi_n d\tau$. In general the evaluation of the integral is rather difficult because ψ_m^* and ψ_n are complicated expressions even for the simplest hydrogen atom. However, it should be pointed out that integral in (12) or (13) turns out to be exactly zero in a large number of cases. It is exactly those transitions, for which these integrals are zero, which are described as forbidden transitions by the selection rules of dipole radiation. The underlying principles of the arbitrarily written selection rule is now apparent, since it corresponds to the evaluation of the integral $\int \psi_m^* e\bar{r}\psi_n \, d\tau$. The following illustration may help in understanding the above.

In terms of spherical coordinates the position vector $\bar{r}$ can be expressed as

$$\bar{r}=r(\sin\theta \cos\varphi \hat{i}+\sin\theta \sin\varphi \hat{j}+\cos\theta \hat{k})$$

$$=r[\sin\theta \frac{1}{2}(e^{in}+e^{-i\varphi})\hat{i}+\sin\theta \frac{1}{2}(e^{i\varphi}-e^{-i\varphi})\hat{j}+\cos\theta \hat{k}]$$

$$=\sum_{p=-1}^{1} a_p(r,\theta)e_{ip}$$

The wave function ψ of quantum states, n, l, m can be written as

$$\psi_{n,l,m}=A_{n,l}(r,\theta)e^{im\varphi}$$

and

$$d\tau=r^2\sin\theta \, dr \, d\theta \, d\varphi$$

Then $\mu=(n', l', m' \mid e\bar{r} \mid n, l, m)=\int \psi_{n',l',m'}^* e\bar{r}\psi_{n,l,m} d\tau$

$$=\sum_{p=-1}^{1} B_p(r,\theta)\int_0^{2\pi} e^{-im'\varphi}e^{ip\varphi}e^{im\varphi}d\varphi$$

$$=\sum_{p=-1}^{1} B_p(r,\theta)\int_0^{2n} e^{(-m'+m+p)\varphi}d\varphi$$

The last integral is zero unless $m-m'=p$. Since p runs from -1 to l_n it is seen that $\Delta m=0, \pm 1$, which is in correspondence with the selection rules.

Suppose a sample containing electron spins at ground level is suddenly exposed to a magnetic field H, one then expects that a certain time will elapse before the magnetization reaches its equilibrium value. Obviously, the electron spin system resides initially in a relatively weak magnetic field of earth before being exposed to the external magnetic field H; hence, the Boltzman distributions for the two states $(2S+1=2)$ having different Zeeman energy are almost exactly one and the spins are practically equally populated between the two levels. If the spin system is suddenly exposed to a strong magnetic field of a few thousand gausses, the spin populations of the two levels will remain approximately equal immediately after the thrust of strong magnetic field. In the field of H, the spins will tend to attain a new thermal equilibrium by redistributing the level populations according to Boltzman distribution. Casimir and Du Pre' (1938) assumed that, even in absence of thermal equilibrium, the distribution over the energy levels of the insolated spin system is given by Boltzman distribution corresponding to a temperature T_s, the spin temperature, which may, however, be different from the temperature of the lattice, which is in turn in thermal equilibrium with the surroundings. Since the ratio of the populations of the two levels is $e^{\frac{g\mu_B H}{kT}}$ under large field H and can be nearly unity immediately after the thrust of H only if the temperature $T=T_s$ of the spin system is very high at large H. This means the spin temperature T_s is not in thermal equilibrium with the lattice temperature. To reach the thermal equilibrium more spins in the upper energy level must make transitions to the lower energy level by one means or another so that the energy of transition may be released in order to lower the spin temperature T_s. This transfer of heat energy is described as the interaction between the spins and the lattice of vibrating atoms or molecules, and the characteristic time required for the excess energy to be transferred to the lattice in order to attain thermal equilibrium is called spin-lattice or thermal or longitudinal

relaxation time, T_1.

when the collection of spins attains detailed equilibrium conditions between levels 1 and 2, we have

$$N_1W_{12}=N_2W_{21}$$

where N_1 is the equilibrium population of Zeeman level 1, N_2 that of level 2, W_{12} stands for the total probability per second that a spin will make a transition from 1 to 2, and W_{21} from 2 to 1. Assuming the level 2 is the upper energy or antiparallel state E_2, one sees that the ratio N_1 to N_2 is larger than unity. Under equilibrium conditions the Boltzmann distribution states that

$$\frac{N_1}{N_2}=\frac{W_{21}}{W_{12}}=e^{\frac{E2-E1}{kT}}=e^{(\frac{2\mu H}{kT})}=e^{(\frac{h\nu}{kT})} \tag{21}$$

Consequently, the emission probability W_{21} exceeds the absorption probability W_{12} and the excess should be just the Einstein spontaneous transition probability. This is consistent with the result of quantizing the lattice phonon field (Sommerfeld and Bethe 1933):

$$\frac{W(\text{emission})}{W(\text{absorption})}=\frac{N_\nu+1}{N^\nu}=e^{(\frac{k\nu}{kT})} \tag{22}$$

Since the phonons obey Bose statistics, we have the relation

$$N_\nu=\frac{1}{e^{(\frac{h\nu}{KT})}-1} \tag{23}$$

According to equation (21), we can let

$$W_{12}=p \tag{24}$$

$$W_{21}=pe^{\frac{2\mu H}{kT}} \tag{25}$$

where p is the stimulated emission or absorption probability per unit time of equation (14). Since the total probability of a single transition from 1 to 2 is the probability of stimulated absorption, equation (24) is justified. Let N be the total number of spins per unit volume and N_e that of excess spins in the lower state per unit volume, then

$$N=N_1+N_2 \tag{26}$$

$$N_e=N_1-N_2 \tag{27}$$

Then, in accordance with the definition of the probability per unit time,

$$\frac{dN_e}{dt}=2(N_1W_{12}-N_2W_2), \tag{28}$$

The factor 2 arises from the fact that the excess number N_e change by 2 for each transition. Substituting equations (24) and (25) with the stipulation that $2\mu H \ll kT$, then

$$\frac{dN_e}{dt}=2p[N_1-N_2-N_2\frac{2\mu H}{kT}]$$

$$=2p[N_e-N\frac{\mu H}{kT} \qquad (29)$$

Equation (29) is true, since $2N_2 \doteq N$ for $2\mu H \ll kT$. Multiplying equation (29) by μ and using the relations

$$N_e\,\mu=M, \quad \frac{N\mu^2 H}{kT}=M_o.$$

one obtains the basic differential equation of paramagnetic relaxation in the form

$$\frac{dM}{dt}=2p(M-M_o) \qquad (30)$$

where M_o is the equilibrium magnetization.

The solution of equation (30) is

$$M=M_o(1-e^{-2pt}) \qquad (31)$$

and hence the spin-lattice relaxation time is

$$T=\frac{1}{2p} \qquad (32)$$

This is the time required for all but 1/e of the equilibrium excess number of spins to reach the lower energy state.

In magnetic resonance arrangement the spin system is exposed to both a static field H and a small oscillating field H_1 perpendicular to H. The small transverse oscillating field H_1 will cause the spins to precess about H and produce a transverse component of M. The spin-spin interaction, which effectively produces a local field originating from neighbors at each electron, distributes the precession frequencies of the spin over a range. Since the spins see different local fields at different times and precess with differente frequencies, it is reasonable to expect that the transverse component of M will statistically have decayed to zero because of the random phase of the spins. We may anticipate a spin-spin or transverse relaxation time T_2 which is a measure of the characteristic time of decay of the transverse component, or that for

establishing phase incoherence among the spins. This spin-spin relaxation time T_2 may be distinct from the spin-lattice relaxation time T_1, which is a measure of the characteristic time for the parallel component to approach its final value.

To have a rough estimate of the value of the spin-spin relaxation time, the Heisenberg uncertainty relation $\Delta E \Delta t = \hbar$ is used, then

$$T_2 = \Delta t = \frac{\hbar}{\Delta E} = \frac{\hbar}{\hbar \Delta \omega} = \frac{1}{\Delta \omega} \tag{33}$$

This relates the line width and the spin-spin relaxation time T_2. Another way to interpret T_2 is as follows. Because of the disbutitrion of local field which each spin experiences, the precession rate of each spin will spread over according to certain distribution functions $g(\omega)$. The trnsverse magnetization component M_T must decay at a rate governed by this distribution in precessional frequencies. Imagine each of a group of N spins of moment μ is aligned at time $t=0$, the moment at latter times will be

$$M_T = N\mu \int_{-\infty}^{\infty} e^{-i\omega t} g(\omega) d\omega \tag{34}$$

Assuming a Lorentzian distribution for $g(\omega)$ together with the normaliztion $\int_{-\infty}^{\infty} g(\omega) d\omega = 1$, we obtain

$$M_T = N\mu \int_{-\infty}^{\infty} e^{i\omega t} \left[\frac{\Delta \omega}{\pi} \frac{d\omega}{(\omega - \omega_0)^2 + (\Delta \omega)^2} \right] \tag{35}$$

where $\Delta \omega$ is the half-width at half-maximum. Evaluation of the integral yields

$$M_T = N\mu e^{-i\omega_0 t} e^{-\Delta \omega t} \tag{36}$$

Hence, the magnitude of the transverse magnetization decays with a time constant $T_2 = \frac{1}{\Delta \omega}$, which is in agreement with the expression (33). It is clear that both T_1 and T_2 are among the factors affecting the line width. One sees that T_2 here is related to the spin wave "packet" (Portis 1953); that is, T_2 is the true "coherence time" of the spin system, the reciprocal of each "packet". Another transverse relaxation time T_2^* is usually defined as the reciprocal line width of a

directly measurable spectroscopic line. In general, $T_2^* \leq T_2$, since all line-broadening effects are included in T_2^*. It will be seen later that the magnitude of T_2 may be interpreted operationally in determining the threshold conditions for achieving fast passage in two-level Masers.

In a simple two-level spin system subjected to microwave excitation, the rate of change of spin populations n_1 and n_2 in lower energy level 1, and upper energy level 2 can be approximately described by the following relations:

$$\frac{dn_2}{dt} = w(n_1 - n_2 - N_e) + p(n_1 - n_2) \tag{37}$$

$$\frac{dn_1}{dt} = -w(n_1 - n_2 - N_e) - p(n_1 - n_2) \tag{38}$$

where N_e is the equilibriun difference population,

w is the probability of the system to "relax" from a given population difference $(n_1 - n_2)$ to the thermal equilibrium population under the influence of spin-lattice relaxation mechanism

p is the induced transition probability of emission or absorption. If the system is in thermal equilibrium with the surroundings, $(n_1 - n_2) = N_e$. Under such conditions stimulation by radiation will result in a net absorption rate given by $2N_e p$. In order to obtain stimulated emission of radiation, n_2 must be greater than n_1, and the system must be put in a state of "negative temperature" according to the equilibrium distribution $\frac{n_2}{n_1} = e^{-\frac{h\nu}{kT}}$ Purcell and Pound (1951) first succeeded in the inverison of a nuclear spin system in a non-adiabatic fashion, and they described the inverted thermal distribution of spin population as at a "negative temperature". The first unsuccessful attempt to invert the electron spin system by the technique of adiabatic fast passage, used by Bloch (1946) in nuclear induction, was performed by Combrisson, Honig, and Townes (1956) using paramagnetism of p-donor spins of phosphorus-doped silicon. The key to the successful experiment of Purcell and Pound is found in the long relaxation times of the nuclear spin system of the lithium floride (LiF) crystal they used. The reported spin-lattice time T_1 and spin-spin relaxation time T_2 at a temperature arouud 1^oK are about 15 seconds and $\frac{1}{50}$ of a millisecond (even in zero

field) respectively. The latter time is sufficiently long since a small magnetic field can be reversed in a much shorter interval. At room temperature the Li^7 spins of a crystal LiF showed a spin-relaxation time of several minutes which is quite independent of the magnetic field in which the crystal is present. The reason for the unsuccessful attempt of Combrisson et al in the electron spin case is that the relaxation times of the phosporous-doped silicon crystal they used are too short because of the inhomogeneous broadening due to isotopic impurity of silicon. Feher, Gordon, Buehler, Geve, and Thurnond (1958) later succseded in the inversion of an electron spin system, using also the phosphorus doped silicon, by lengthening its relaxation times or narrowing its line width through the use of a crystal of isotopically purified silicon. As a result the condition of oscillation was satisfied and a spontaneous emission of radiation was obtained from the electron spin system. Chester, Wagner, and Castle (1958) operated successfully a two-level solid-state Maser using single crystals of quartz and of magnesium oxide, each irradiated with neutrons to introduce paramagnetic defects. Inversion of the electron spin population was achieved by Chester et al using the technique of adiabatic fast passage in which the magnetic field was swept through resonance.

One of the methods of obtaining the state of spin inversion or negative temperature is termed as non-adiabatic field reversal. It is obvious that this technique of achieving negative temperature for spin system can be applied to electronic case on the condition that the field reversal can be accomplished within a time which is short in comparison with the spin-spin relaxation time of the electron spin-system in question. This sudden field reversal in the electron spin system is not as easy as that in the nuclear spin system since the spin-spin relaxation time of the former is usually much smaller than the latter. Although this technique has the advantage of requiring no microwave field, no practical application of the technique has been carried out yet because of the difficulty involved in very short time of field reversal.

An alternative method of spin inversion is the adiabatic fast passage technique, first introduced by Bloch (1946) in nuclear induction study. In this method coherent microwave power of precessional frequcncy ω_0, with its magnetic field H_1 perpendicular to the static magnetic field H, is introduced into the tuned cavity containing the paramagnetic substance. There are two ways to achieve spin inversion in this technique: (1) The frequency of the microwave field starts far off resonance and is slowly swept through the resonance frequency until it is far off resonance on the other side, and (2) The d-c magnetic field starts far off resonance and is slowly swept through resonance until it is far off resonance on the other side. The sweeping of magnetic field H is entirely equivalent to that of frequency ω. In both cases, inversion of the spin system results, whichever the direction of sweep. In order to understand the phenomenon and to derive the limiting conditions, it is instructive to adopt the coordinate system rotating at an angular frequency ω_0 with respect to the laboratory system (Rabi, et al 1954). Suppose H is slowly swept through resonance from H_i (initial) to H_f (final), where both H_i and H_f are far off from the resonance value $H=\frac{\omega_0}{\gamma}$ (γ is called the gyromagnetic ratio). The following diagrams will give a clear physical picture of the phenomenon during the whole passage.

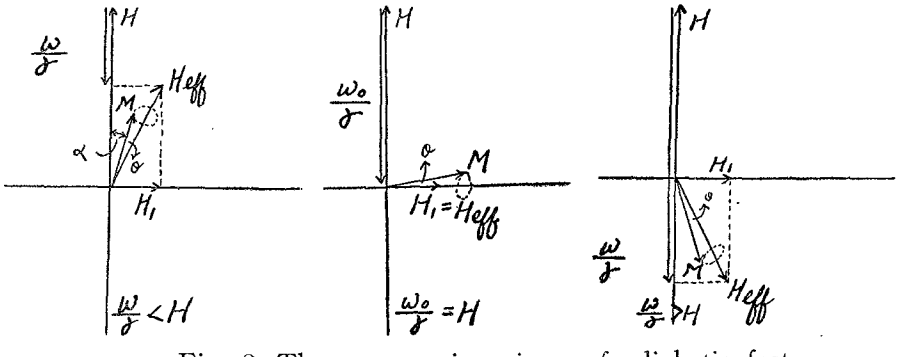


Fig. 2. Three successive views of adiabatic fast passage in rotating coordinates. (H sweeping through resonance.)

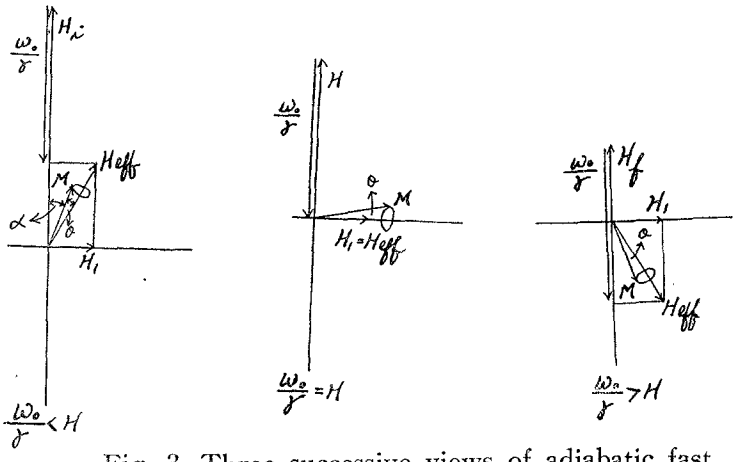


Fig. 3. Three successive views of adiabatic fast passage in rotating coordinates. (ω sweeping through resonance).

The resultant effcetive field, $H_1 + (H + \frac{\omega}{\gamma})$, seen by the spin system in the rotating coordinates, behaves in the manner depicted in Figs 2 and 3 during the fast passage The magnetization vector M innitially aligned in the direction of H will now precess about H_{eff} at the Larmor frequency, where

$$\Omega = \gamma\ H_{eff} = \gamma\sqrt{H_1^2 + (H + \frac{\omega}{\gamma})^2}$$

when H sweeps through resonance, $H = H(t)$ is a function of time. In order that the spin inversion may occur in adiabatic fashion it is necessary that the time required for the precession of the magnetization M about the effective field H_{eff} must be short in comparison with the time required to sweep H through the resonance. In other words, M will follow the changes in H_{eff} adiabatically if M nutates many revolutions about H_{eff} for each infitesimal change of H_{eff}. Under such conditions M can closely trail H_{eff} without getting lost and the angle θ between M and H_{eff} can be maintained approximately constant in order ensure inversion. The time required for the nutation of N about H_{eff} is $t = \frac{2\pi}{\Omega} = \frac{2\pi}{\gamma H_{eff}}$, and that for the passage $t_p = \left|\frac{H_{eff}}{\frac{dH_{eff}}{dt}}\right|$. Accordingly,

$$\frac{2\pi}{\gamma H_{eff}} \ll \left|\frac{H_{eff}}{\frac{d\,H_{eff}}{dt}}\right| = \frac{H_{eff}}{\left|\frac{dH}{dt}\right|}$$

or
$$\left|\frac{dH}{dt}\right| << \frac{\gamma(H_{eff})^2}{2\pi} \tag{39}$$

Since the minimum value of H_{eff} is H_1, the adiabiatic condition can be written as

$$\left|\frac{dH}{dt}\right| << \gamma H_1^2. \tag{40}$$

The condition of equation (40) can also be derived in slightly different arguments. This will be done in order to have more insight into the problem. In order that M can follow closely the change of H_{eff} in directions' it is necessary that the change of the angle of nutation φ about H_{eff} be large during the period of passage t_p; i.e,

$$\varphi = \Omega t_p >> 1$$

or
$$(\gamma H_{eff})\left(\frac{H_{eff}}{\frac{dH_{eff}}{dt}}\right) >> 1 \tag{41}$$

which is equivalent to (39) and (40). To state the problem in yet another way, one can say that in order to have proper spin reversal, the angular velocity of the nutation of M about H_{eff}, $\frac{d\varphi}{dt}$. must be much faster than the angular velocity of H_{eff}. $\frac{d\alpha}{dt}$, where α is the angle between H and H_{eff}. Hence, one requires

$$\frac{d\varphi}{dt} = \Omega = \gamma H_{eff} >> \frac{d\alpha}{dt} \tag{42}$$

but

$$\tan\alpha = \frac{H_1}{H(t) - (\frac{\omega_0}{\gamma})}$$

and

$$\frac{d\alpha}{dt} = \frac{H_1}{(H_{eff})^2}\left|\frac{dH(t)}{dt}\right| = \frac{H_1}{(H_{eff})^2}\left|\frac{dH}{dt}\right|.$$

Therefore

$$\gamma H_{eff} >> \frac{H_1}{H_{eff}}\left|\frac{dH}{dt}\right| \tag{43}$$

which is again in accord with equations (39) to (40). Thus, if H and H_f are taken suffciently far off the resonance value, then θ, being small initially, remains small at the end of the "slow" passage and substanially complete inversion of the magnetization vector M will result. This adiabatic condition given by equation (40) imposes an

upper limit on the sweep rate, and it will be shown that the lower limit is fixed by the transverse relaxation machanism.

To simplify the explanantion, let the inhomcgeneous broadening be neglected so that the total transverse relaxation time is just T_2. Furthermore, let the spin-relaxation time T_1 be neglected also since T_1 usually is much larger than T_2. it is clear that during the passage through resonance transverse magnetization must be present because of the inversion. Then, in order to invert M successfully in adiabatic fashion, it is necessary that the passage time t_p, during which M has non-negligible transverse components, be small compared to T_2 Hence,

$$t_p = \frac{H_{eff}}{\frac{dH_{eff}}{dt}} = \frac{H_{eff}}{\left|\frac{dH(t)}{dt}\right|} \ll T_2. \tag{44}$$

The maximum of the transverse component of H_{eff} is H_1 hence,

$$\left|\frac{dH}{dt}\right| \gg \frac{H_1}{T_2}. \tag{45}$$

This, together with the adiabatic condition of equation (40), leads to the requirement on the rate of the passage:

$$\frac{H}{T_2} \ll \left|\frac{dH}{dt}\right| \ll \gamma H_1^2. \tag{46}$$

In turn the following restriction on H_1 is imposed according to the inequalities of equation (46):

$$\gamma H_1 T_2 \gg 1 \quad \text{or} \quad H_1 \gg \frac{1}{\gamma T_2}. \tag{47}$$

The interpretation of the equation (47) is that the microwave field H_1 must be larger than the line width of the resonance in gauss. It is recalled that equation (47) is derived by assuming no inhomogenceus broadening and accordingly the "line width" here is meant the "packet width". Since $\gamma \cong = 2 \times 10^7$/gauss-sec. for electron spin system, we have

$$H_1 \gg \frac{5 \times 10^{-8}}{T_2} \text{ gauss} \tag{48}$$

with T_2 in seconds.

Another requirement in connection with the relaxation time T_1 may be necessary if T_1 is smaller than T_2^* (including effects due to inhomogeneous broadening). In this case the passage time must be small

compared with T_1 so that the inversion is completed before the competing relaxation processes can restore the system to thermal equilibrium.

The effect of radiation damping in the process of spin inversion must be mentioned here. When a spin system is exposed to a microwave field, there is a reaction due to the coupling of the spin system and its own radiation field. In order to ensure population inversion, the driving field H_1 must be much larger than the maximum radiation field of the spin system. In such case the spin system will continue to follow the driving field even in the event of complete destructive interference between the driving field and radiation field. Bloom (1957) has given a detailed analysis on the effects of radiation damping on spin dynamics.

The method of achieving the state of spin inversion or negative temperature in a three-level solid-state Maser as proposed by Bloembergen (1956) is to saturate the transition between the outer pair of levels in order to obtain population inversion between the inner pair of levels. The three unequally spaced energy levels are related as follows: $E_3 > E_2 > E_1$. The resonance freqnencies are:

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

If the system is pumped at frequency ν_{31} and signal frequency is ν_{32}, results anologaus to equations (37) and (38) are obtained:

$$\frac{dn_3}{dt} = W_{13}(n_1 - n_3 - N_{13}) + W_{23}(n_2 - n_2 - N_{23}) + p_{31}(n_1 - n_2) + p_{32}(n_2 - n_3)$$

$$\left.\begin{aligned} \frac{dn_2}{dk} &= W_{23}(n_3 - n_2 - N_{32}) + W_{21}(n_1 - n_2 - N_{12}) + p_{32}(n_3 - n_2) \\ \frac{dn_3}{dt} &= W_{13}(n_3 - n_1 - N_{31}) + W_{21}(n_2 - n_1 - N_{21}) + p_{31}(n_3 - n_1) \end{aligned}\right\} \quad (49)$$

Where N's are the equilibrium difference population between a corresponding pair of levels,

p's are the stimulated absorption and emission probabilites between a corresponding pair of levels,

W's describe the tandency to "relax" from a given population unbalance to the equilibriam unbalance between a corresponding pair of levels.

If the pumping at frequency ν_{31} saturates and therefore equalizes the populations of levels 1 and 3, the population n_3 is now larger than the population n_2. Accordingly the state of "negative temperatine" is obtained between levels 3 and 2 and Maser action exists between these two levels. For the conditions $W_{31} >> W$'s and p_{32}, the steady-state $(\frac{dn_1}{dt} = \frac{dn_2}{dt} = \frac{dn_3}{dt} = 0)$ solutions give the required population unbalance $(n_3 - n_2)$. This population unbalance will be positive, corresponding to stimulated emission at freqnency ν_{32}. Many three-level solid-state Masers have been operated with success by this "pumping" technique. The chief advantage of the three level Maser lies in the fact that it offers continuous operation, while the two-level Maser can only have an intermittent performance.

Present Status

Even though this quantum-mechanical device is still in its infant stage, considerable attention has been directed toward it in both the research and development phases. One of the major interests in Maser amplification lies in the fact that the amplification thus obtained has extremely low excess noise. Thus Masers offer the possibility of greater ultimate sensitivity in the fields of radio astronomy, radar, communication etc. In addition, Masers can be designed to oscillate at an extremely stable frequency and thus provide the means for very accurate time standards. In addition to its technical improvement in the engineering aspect, research effort has been emphasized in search of suitable paramagnetic substances for Maser operation. In the last decade, although tremendous amounts of activity have been directed into the paramagnetic resonance research, the information relevant to the materials useful for Maser operation is surprisingly scarce. This is mainly due to the fact that the frequencies of transition are of primary interest in paramagnetic resonance. Knowledge of spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 of paramagretic materials is

important in choosing Maser materials. An accarate theory for evaluating T_1 and T_2 is not available yet whereas measurements of T_1 are rather difficult and values of T_1 are therefore usually reported by order of magnitude. Since most paramagnetic resononces are inhomogeuonsly broadened, the reported spin-spin relaxation times are always T_2^* (spin-spin relaxation time with inhomogeneous broadening) and not T_2. Knowledge of T_2 is important in determining the feasibility of inversion by adiabatic fast passage technique.

Feher (1958) succeeded in obtaining spontaneous emission of radiation from electron spins of doped silicon, wherear Chester et al (1958) using F centers (MgO irradiated by neutrons) succeeded in operating a two level Maser. Although two paramagnetic salts (a crystal of lanthanum ethyl sulphate doped with gadolinium ions, and a crystal of potassium cobalti-cyanide doped with chromium ions) have been used in the successful operation of three-level Masers, successful two-level Maser using paramagnetic salts has not been reported yet. Comparatively speaking, the requirements for the choice of material for two-level Masers is less stringent than those for three-level Masers, since the ratio of pumping frequency and signal frequency is more or less restricted by available microwave microwave generators and equipment. However, the fact that an exact information of T_2 is important in the adiabatic fast passage technique for two-level Masers, makes the selection of material for two-level Masers rather aimless because T_2 has not been investigated at all for almost all paramagnetic salts. In addition the conditions of equation (46) for adiabatic fast passage are usually very difficult to satisfy in an electron spin system. Another difficulty is that the relaxation times generally encountered in electron spin systems are much too short. In most cases electron spin resonances are inhomogeneously broadened for various reasons and therefore yield rather short T_2^* 's. Combrisson et al (1956) could not invert the spins of doped silicon because of too short T_2^*, while Feher et al (1958) obtained the spin inversion in the same material by lengthening T_2^* through isotopic purification of the silicon

sample. Usually T_1 can be lengthened by reducing the concentration of paramagnetic spins.

It is clear that further development of Masers leans heavily on the research of paramagnetic substances suitable for Maser performance.

REFERENCES

Artman, J. O., Bloembergen, N., and Shapiro, S., *Phys. Rev.*, Vol. 109, P. 1392, (1958)

Autler, S. H., and McAvoy, N., *Rhys. Rev.*, Vol. 110, p. 280, (1958)

Bloch, F., Hansen, W. W., and Packard, M, *Phys, Rev.*, Vol. 69, p. 127, (1946).

Bloom, S., *Jour. Appl. Phys.* Vol. *28*, p, 800, (1959).

Bosov, N. G., and Prokhorov, A. M., *J. Exptl. Theoret. Phys.* (U. S. S. R.), Vol. 27, p. 431, (1954); *J. Exptl. Theoret. Phys.*,(U. S. S. R.), Vol. 28, p. 259, (1955a).

Belz, M. H., *Phil. Mag.*, Vol. 44, p. 479, (1922).

Bloch, F., *Phys, Rev.*, Vol, 70, p, 460, (1956).

Bloembergen, N., Purcell, E. M., Pound, R. V., *Phys. Rev.*, Vol. 73, p. 679, (1948).

Bloembergen, N., *Phys.* Rev., Vol. 104, p. 324, (1956).

Casimir. H. B., and Du Pre', *Physica*, Vol, 5, p. 507, (1938).

Chester, P., Wagner, P., and Castle J., *Phys. Rev.*, Vol. 110, p. 281, (1958).

Cleeton, C. W., and Williams, *N. H.*, *Rhys. Rev.*, Vol. 45, p. 234, (1934).

Combrisson, J., Honig, A., and Townes, C, H., *Compt. Rend.*, Vol. 242, p. 2451, (1956).

Feher, G., Gordon, J, P., Buehler, E., Gere, E, A., and Thurmond, C. D., *Phys, Rev.*, Vol, 109, p. 224, (1958).

Gort^{e}r, C. J., *Physica*, Vol. 3, p. 505, (1936).

Cordon, J. P., Zeiger, H. J., and Townes, C. H., *Phys. Rev.*, Vol. 99, p. 1264, (1955).

Karplus, R., and. Schwinger, J., *Rhys. Rev.*, Vol. 73, p. 1020, (1948).

Kittel. C., Nuovo Cimento, No. 3, del Supplemento al Vol. 6, p. 895, (1957).

Kingston, R. H., *Proc. I. R. E.*, Vol. 46, p. 916, (1958)

Kravendonk, J. V., and Van Vleck, J. H., *Rev. of Modern Phys.*, Vol. 30, p. 1, (1958).

Lasarew, B., and Schubnikow, L., *Physik, Z. Sowjetunion,* Vol. 11, p. 445, (1937).

Makov, G., Kihuchi, C., Lambe, J., and Terhune, R., *Phys. Rev.*, Vol. 109, p. 1399, (1958).

McWhorter, A. C., and Meyer, J. W., *Phys. Rev.*, Vol. 109, p. 312, (1958).

Pauli, W., *Z. Physik,* Vol. 41, p. 81, (1927).

Portis, A, M., *Phys. Rev.*, Vol. 91, *p.* 1071, (1953)

Purcell, E. M., and Pound, R. V., *Phys. Rev.*, Vol. 81, p. 279, (1951).

Purcell, E. M., Torrey, H. C., and Pound, R. V., *Phys, Rev.*, Vol. 69, p. 37, (1946).

Rabi, I. I., *Phys. Rev.*, Vol. 51, p. 652, (1937).

Rabi, I. I., Zacharias J. R., Millman, S., and Kusch, P., *Phys. Rev.*, Vol., 53, *p.*318., (1938).

Rabi, I. I., Ramsey, N. F., and Schwingar, J., *Rev. Modern. Phys. Vol. 26,* p. *167, (1954).*

Van Vleck, J.H., *Phys. Rev.*, Vol. 71, p. 413, (1947); *Nuovo Cimento,* Vol. 6, Supplemento No. 3, p. 933, (1957).

Scovil, H. G. D., *Trans. I. R. E.*, PGMTT-6, p. 29, (1958).

Scoril, H, G. D., Feher. G., and Seidel. H., *Phys. Rev.*, Vol. 105, p. 762, (1957)

Sommerfeld, A., and Bethe, H. A., *Handbuch der Physik,* Vol. 24, Part 2, p. 500, (1933)

Waller, L., *Z. Phys.*, Vol. 79, p. 370, (1932).

Weber, *Trans.*, J., *I. R. E.* PGED-3, p. 1, (1953).

Wittke. J. P., *Proc. I. R. E.*, Vol. 45, p. 291, (1957)

Zavoisky, E., *J. Physics,* (U. S. S. R.,) Vol. 9, p. 211, 245, 447, (1945.)