INSTRUMENTATION OF MICROWAVE ELECTRON RESONANCE IN MAGNETIC FIELDS *

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Introduction

The title of this paper is long and descriptive, but the phenomena studied are known as paramagnetic resonance or ferromagnetic resonance, as the case may be. The device which is used to perform these studies is known as a paramagnetic spectroscope, and is described in the following pages.

The magnetic resonance of electrons is largely studied for the information that it yields about matter in the solid state. The physicist gains information concerning energy levels of electrons in solids, crystal fields, luminescent activators, ferromagnetism, and semi conductors, while the chemist may be enlightened concerning bond types, biradicals and F-centers. At the present time, the study of electron resonance is mainly the domain of the basic researcher; however, some commercial applications have been announced. Two devices utilizing the electron resonance principle are the microwave gyrator and the microwave variable attenuator or amplitude modulator. The full story of the mechanism of magnetic resonance absorption is very complicated, however, a few simplified details are necessary to an understanding of the paramagnetic spectroscope.

Electrons are the commonest of particles found in the universe, but they display magnetic resonance only in certain special substances. Electrons have two inherent properties in addition to charge and mass which are necessary for an understanding of resonance; they are spin and magnetic moment. The spin is an angular momentum quantity from quantum mechanics, and magnetic moment describes the fact that the electron has magnetic polarity, much the same as a small bar magnet. These properties are elusive and not commonly observed because most matter is made up of electrons that pair off two by two in such a way that, as far as external measurements are concerned, their effects are cancelled out. This is known as antiparallel coupling of the electrons. The exceptional cases are those of certain free atoms, ferromagnetic substances, and some paramagnetic substances which usually contain an odd number of electrons. The odd number means that at least one electron must be unpaired and its undiminished magnetic properties may be detected by external measurements. Consider now the problem of a spinning body having a magnetic moment and placed in a strong magnetic field, and then subjected to a torque. A simplified mechanical analogy is that of a gyroscope spinning in a frame in the earth's gravitational field to which a torque is applied. The gyroscope moves in a direction at right angles to the torque and in fact precesses -- so it is with the electron.

Some of the equations necessary to describe the precession of a gyroscope look on the surface like some of the equations used to describe the motion of a spinning electron in a magnetic field. The electron tries to line up with the magnetic field, much as a small magnet would, but instead, its

* Presented at the I.R.E. Western Electronics Show and Convention in San Francisco, August 21, 1953.

axis precesses around a line of force at a frequency known as the gyromagnetic frequency. All of the unpaired electrons in a material so placed in such a field process at the gyromagnetic frequency, but in random phase so the net effect external to the sample is zero. If the precessing electrons are, in addition, placed in an alternating magnetic field of the same frequency, they may be made to fall in step with the alternating field. Increasing the orderliness of the precessing electrons requires an increase of energy in the system. This additional energy is supplied by the oscillating field. Clearly for maximum effect, the oscillating field must lie in a plane perpendicular to the lines of magnetic force about which the electrons are precessing. The absorption of energy by the system is measured and automatically recorded. The relation between the strength of the steady magnetic field and the frequency of the oscillating field is such that the former equals a constant times the latter. When the steady field strength is of the order of 3400 gauss the oscillating field frequency falls in the X-band microwave region. Hence the name microwave paramagnetic spectroscope or microwave spectroscopy.

The Overall System

The components necessary in a system for detecting paramagnetic resonance absorption will now be described in general (See Fig. 1). The basic requirement is that of a strong, steady magnetic field and a comparatively weak oscillating magnetic field of the proper frequency perpendicular to one another. As mentioned previously, convenient values are a frequency in the X-band range and a steady field of about 3300 gauss. The source of the radio frequency energy is a klystron oscillator feeding a resonant cavity sample chamber. The sample chamber is oriented between the poles of an electromagnet such that the perpendicular field requirement is satisfied. The amount of microwave energy passing through the sample cavity is measured in the crystal detector. As the steady magnetic field is increased through the valve required for resonance, the microwave detector will indicate a decrease in received power. A plot of received constant frequency microwave power vs. magnetic field strength is the paramagnetic spectra for whatever material is in the sample cavity. A constant field-variable frequency plot would provide the same information, but at microwave frequencies, it is far simpler to hold the frequency constant.

The system as described up to now is such as to require direct current amplification after the microwave detector because the large inductance of the magnet coil demands a slow field change. In practice, a change of 500 gauss is made in about four minutes. Direct current amplification is not feasible except for materials showing very large absorption spectra and is to be avoided because of its inherent stability problems. To circumvent the dc amplifier problem, a method of slope detection is used. Superimposed on the very slow change of magnetic field strength is a modulation of amplitude of one to five gauss at a frequency of 32 cycles per second. This is accomplished by adding a set of sweep coils to the magnetic circuit of the electromagnet and driving them from an audio power amplifier. By this method, the amplitude of 32 cycle signal present in the output of the microwave detector is proportioned to the slope of the absorption curve since the sweep amplitude is kept to a small fraction of the curve width. Thus amplitude detection of the 32 cycle signal gives a plot of the derivative of the absorption curve vs. field strength. The lower limit of frequency at which the sweep coils are driven is determined by the desire to use ac amplification and the upper limit by their inductance. After ac amplification and detection, the absorption information is given dc amplification and is then recorded on a Brush dual pen chart recorder.

The other quantity that must be measured and recorded is magnetic field strength. The most satisfactory and precise method of measuring magnetic field is with the nuclear fluxmeter. This instrument operates on the same type of resonance absorption principle as previously discussed for the electron, except that the radio frequency energy is taken up by atomic nuclei instead of electrons. The Pound Nuclear Fluxmeter, made by Laboratory for Electronics, uses hydrogen nuclei or protons as the absorbing medium. Protons in magnetic fields of the order of 3300 gauss show absorption of energy when the radio frequency is of the order of 14 mc. Thus measurement of the proton resonance frequency gives precise information as to the strength of the magnetic field. The magnetic field is measured by having the proton sample next to the microwave sample cavity and always tuned to resonance by a servo system. Because the servo system keeps the proton resonance condition satisfied, it is only necessary to measure the frequency of the proton oscillator during the course of the run. The details of how this is done and recorded will be considered later.

Details of the Microwave Part of the Spectroscope

The microwave system consists of a source of energy, a sample chamber, and a detector. The energy source is a 723 A/B klystron operated from a well-regulated power supply. Careful power supply regulation and long warm up periods provide an essentially monochromatic microwave energy source without recourse to complicated stabilization methods. Fig. 2 shows a schematic diagram of the microwave system. Following the klystron is an attenuator and a 20 db directional coupler. Energy is taken off in the directional arm for frequency measurement by a P.R.D. 551 wavemeter. The frequency is indicated by a dip in crystal current, as read by the microammeter. Most of the paramagnetic work is done with a constant microwave frequency of 9300 mc. The energy that passes through the directional coupler is sent to the transmission cavity sample holder. The cavity operates in the circular electric mode, causing a maximum of rf magnetic field to exist along its central axis.

The TE_{011} mode was chosen, in part because of its low loss or high Q, and, in part, because an aperture for sample illumination and insertion may readily be cut in the end of the cavity opposite the tuning plunger without appreciably disturbing the field. Also this mode satisfies the condition for resonance absorption - rf field perpendicular to the external magnetic field. The sample of material to be studied is placed in the axial field through the use of a special teflon sample holder which fastens to the movable wall of the cavity. The cavity is made entirely of brass (including the micrometer) to avoid distortion of the magnetic field and silver plated to minimize losses. The Q of the transmission cavity is of the order of 15000 with no sample and may be reduced to as much as 50% of this value by some materials. The amount of materials placed in the cavity is dependent upon its absorption intensity, but usually averages about the size of a match head.

Following the cavity is the microwave detector, which consists of a crystal rectifier followed by a movable short. Preceding the detector and also preceding the resonant cavity are movable stub tuners, which match these elements to the line; they are represented on the schematic by movable susceptance symbols. The microwave detector is perhaps the most important element in the system as it is the predominant source of noise. The information taken from the microwave detector is in the form of a 32 cycle signal or carrier, which is in turn modulated by the absorption information. Crystal rectifiers, in general, become quite noisy in the low audio part of the spectrum and vary considerably in noise output from one unit to the next. A screening test was made on all available crystals to select the best ones. Out of 100 units screened, about 10 fell into the "very good" class when the crystals were tested for conversion efficiency and noise output. The "very good" class was considered to be those units with a ratio of conversion efficiency to noise output three or more times the average for the 100 units. The crystals used in the spectroscope operate at an incident rf power level of 1 milliwatt, and were tested at this power level.

The Magnet

The magnet used to supply the steady field has pole pieces eight inches in diameter and a gap of 2½ inches. It is one of a line of research magnets made by Varian Associates of San Carlos, California. The coils are water cooled, and have a dc resistance of approximately 100 ohms. At a maximum current of two amperes in the coils, the field reaches a value of 10,000 gauss. The current range required to cover most spectra (with klystron at 9300 mc) is .40 to .60 amperes. The power supply for the magnet is electronically current regulated and is provided with a motor drive to slowly change the current in the coils during a run.

The observation of spectra containing narrow absorption curves demands a highly homogenous field. The steady value of magnetic field must be constant throughout the volume of the sample, or the spectra will be unduly broadened. With shims the magnetic field may be held to a uniformity of 4 gauss in 4000 over the 4 inch center circular area. The largest samples used in the spectroscope are of the order of ¼ inch across and are placed in the center of the field.

Details of the Electronic Equipment

The absorption information is in the form of an amplitude modulation of the 32 cycle carrier, which is present in the output of the microwave detector. The level at this point in the system is very low and considerable amplification is required before the signal can drive a pen recorder. Also present in the crystal detector output is wide band noise some interference from the 60 cycle line and second harmonic of the line frequency. Because the absorption information comes only at 32 cycles plus side bands of maximum deviation of 1 cycle, much of the noise and extraneous signals may be eliminated by narrowing the bandwidth of the electronic amplifiers.

The electronic system starts with a well shielded (90 db) audio input transformer, which serves to match the crystal detector to the vacuum tube circuits (see Fig. 3). The first bandwidth narrowing is done by an electronic low pass filter which passes flat from 10 to 40 cycles, but is down 20 db at 60 cycles. Following the filter is a Hewlett Packard 450A amplifier which has a gain of either 10 or 100. After this amplification, the signal is divided and applied to two identical narrow band amplifiers. These amplifiers are tuned to the 32 cycle carrier, and have a half power bandwidth of 3 cycles. The square law detector circuit consists of amplification and detection by a bridge rectifier of four 1N35 diodes. The filter network following removes the 32 cycle carrier component, as well as its second harmonic. This is necessary as the Brush recording equipment will respond up to 100 cycles. The information signal, containing frequencies up to about one cycle, is given dc amplification and applied to one pen of a dual pen recorder.

The other arm of the electronic system contains a synchronous or phase sensitive detector. This type of detector is essentially an electronic correlating device which seeks out cyclic information of a particular frequency by comparing the incoming signal with a reference signal of the desired frequency. The source of the reference signal is the same audio oscillator which feeds the sweep coil amplifier. Such a detector is desirable because it is a narrow band device, and also because it retains information regarding the phase of the incoming signal with respect to the reference signal. Since the incoming signal is proportional to the slope of the absorption curve, it may have only two phase values differing by 180°. Thus the phase detector output gives information about the magnitude of the slope of the absorption curve, as well as the sign of the slope. The latter information is very important if the true absorption curve is to be reconstructed from the derivative data. After filtering the carrier components from the phase detector output, the information signal is passed through a dc amplifier and applied to the other pen of the dual channel recorder.

The objective in the design of the spectroscope is to obtain the ultimate in signal to noise ratio. As previously stated, the microwave detector is the predominant noise source in the system. Careful selection of crystals will minimize this noise, but not eliminate it.

Once noise enters the information channel, the problem is one of system design such that the signal is maximized and the noise minimized. The noise has been minimized by collecting information from the sample at a very slow rate (about to to 10 minutes per run) and modulating a low frequency carrier. Furthermore, narrow band amplification has been used at the 32 cycle carrier frequency to give the system a 3 cycle bandwidth.

The use of dc for filaments was not necessary, as the amplifier noise is low relative to the microwave detector noise and because the system is tuned for 32 cycles. However, it is necessary to use dc for the klystron filament.

It might seem that further improvement in signal to noise ratio could be obtained by lengthening the time of the run and appropriately increasing the time constant of the filter network preceding the dc amplifiers. In theory this would be true, but in practice it does not work out so well. A run which takes one to two hours for completion puts demands on the system other than just time constant changes. Namely the problem of long time stability vs. short time stability presents itself. Tests have been made which indicate that the increase of signal to noise ratio is not significant enough to warrant the inconvenience of long time runs. The problems are mainly ones of klystron frequency stability (1 part in 10^5 required for satisfactory run), line voltage variations, and magnetic field stability.

Magnetic Field Measurement

For the absorption information to be useful, it is necessary that the magnetic field strength be recorded on the same chart during the run. The field frequency relation for protons in nuclear magnetic resonance is 4257.76 cycles per gauss and, consequently, a knowledge of frequency means a knowledge of magnetic field strength. As stated previously, the Pound Nuclear Fluxmeter, or Magnetometer as it is called, is kept tuned to the resonance condition throughout the run by a servo system and the frequency monitored. The procedure is to compare the fluxmeter frequency with that generated by a General Radio frequency standard. Such a standard has a carefully stabilized 100 kc crystal driving a multivibrator which generates harmonics up through the frequency range of proton resonance. If these harmonics are mixed with the frequency from the fluxmeter, a zero beat will occur every 100 kc. These zero beats are caused to operate a third marker pen on the Brush dual pen recorder. A 100 kc frequency separation of marker pips corresponds to a magnetic field change of 23.49 gauss. Of course, any other separation could be obtained by changing the crystal frequency. The details of the field measurement system are as follows (See Fig. 4).

The probe containing the proton sample also contains the coil of the rf oscillator and a set of sweep coils with axis perpendicular to the rf coils in the probe. When the resonance condition is satisfied, the protons absorb rf energy from the oscillator coil, thus increasing the losses in the circuit. The sweep coils modulate the steady magnetic field and allow the resonance condition to be swept through cyclicly so the loss or resonance information may be passed through an ac amplifier. If the phase of the output signal is examined, it will be found to change by 180° when passing through resonance. When exactly on resonance, the output signal frequency is double the sweep frequency. This characteristic is used to drive a two-phase ac servo motor coupled to the Magnetometer tuning shaft. One motor winding receives a signal from the sweep coil oscillator that is 90° out of phase with respect to the output signal from the Magnetometer. The servo motor will then drive in opposite directions, according as to whether the fluxmeter is tuned above or below the proton resonance condition. By proper attention to polarity, the motor may be made to keep the fluxmeter always tuned to resonance, even though the steady magnetic field is slowly being changed. In practice the line frequency sweep is avoided and a frequency of 85 cycles used for the magnetometer sweep coils and servo motor. It is well to point out here that the servo amplifer must be tuned to 85 cycles as the steady magnetic field is also being swept by the large sweep coil at a frequency of 32 cycles. This causes a proton resonance signal to be generated at 32 cycles, as well as at 85 cycles, and the former signal must be kept from reaching the servo motor. Tachometer feed back is used to prevent the servo system from hunting about the resonance point due to the inertia of the drive motor and gears.

The zero beats are caused to occur by combining the Magnetometer rf signal with that of the frequency standard in a specially designed mixer amplifier. Such an amplifier must have a pass band of about 4 mc centered about 14 mc as the fluxmeter frequency may vary this much when a broad spectrum is being run. The audio output from the mixer circuit is amplified and passed through a low pass network with adjustable cutoff frequency. The output is rectified and caused to vary the bias of a thyratron which shorts a charged capacitor through the marker pen actuating coil. The low pass cutoff frequency is adjusted to be as low as possible and still fire the thyratron when a zero beat is approached. A 40 cycle cutoff frequency is satisfactory for most runs, but may vary with the speed of changing the magnetic field. The thyratron does not fire exactly on zero beat, but a little ahead. This error is not serious as it helps compensate for the necessary lag in the positional servo system and, furthermore, a one gauss error would mean a beat frequency of 4257.76 cycles.

Because the markers are 100 kc apart, it is necessary to identify only one of them. The procedure is to tune a communications receiver to some frequency in the range to be covered and, when the zero beat is heard, that marker pip is checked by hand to be the set frequency of the receiver. The scope monitor displays the proton resonance and indicates that the servo system is tracking the field properly.

Presentation and Analysis of Data

The paramagnetic spectra come from the Brush recording equipment in the form of a tape from one to five feet long, depending on the speed of the run and the width of the spectra. Fig. 5 is a photograph of a typical data sample. The recorder was slowed down to give the tapes a suitable aspect ratio for slide presentation. Tapes used for measurement have about (5) centimeters between the 23.49 gauss field markers. At the top of the tape, the field marker pips may be seen; every ten pips mean a change of proton resonance frequency of 1 mc. The next lower curve on the tape represents the derivative of the absorption curve also, but without sign preservation. This curve is the result of square law detection of the 32 cycle carrier. The lowest curve is the derivative of the absorption curve, as presented by the phase detector; note the preservation of the sign of the slope. Each curve serves a purpose in that the peaks of the absorption curve are determined by the zero crossing of the phase detector curve, and the width of the curves at maximum slope points is most easily determined from the square law detector curve. The true shape of the curve is not apparent from these charts because of the curvilinear coordinates of the recording mechanism; the curves are actually symmetric.

Field strength information is taken from the recorded spectra by linear interpolation between the check points. Satisfactory interpolation demands a check point spacing of about five centimeters and a recording time of approximately ten minutes for a 1000 gauss spectra. Under these conditions the field value of any absorption line may be determined to one part in five thousand. Much greater accuracy is inherent in the nuclear fluxmeter when used in a point by point determination of the field strength. However, the added convenience of automatic tracking and recording outweighs this additional inherent accuracy. The overall accuracy of the spectroscope is limited to one part in 3300 by measurement of microwave frequency and magnetic field stability.

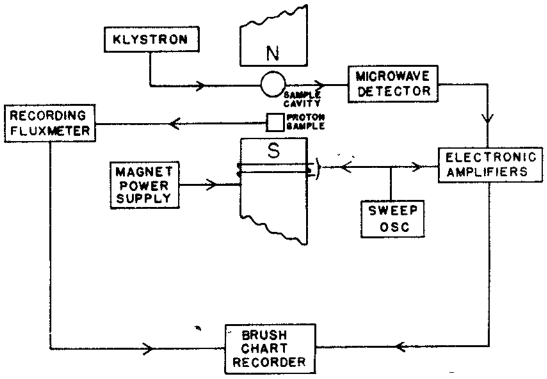

Fig. 1 - Spectroscope block diagram.

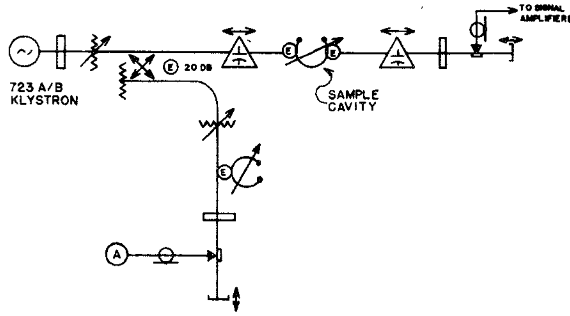

Fig. 2 - Microwave system.

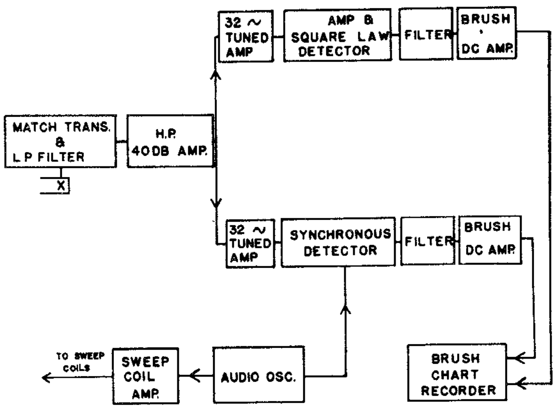

Fig. 3 - Electronic system.

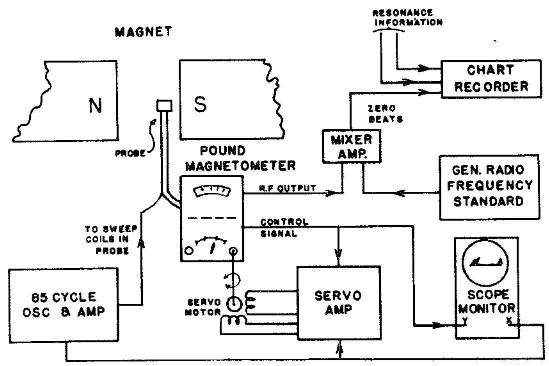

Fig. 4 - Field recording system.

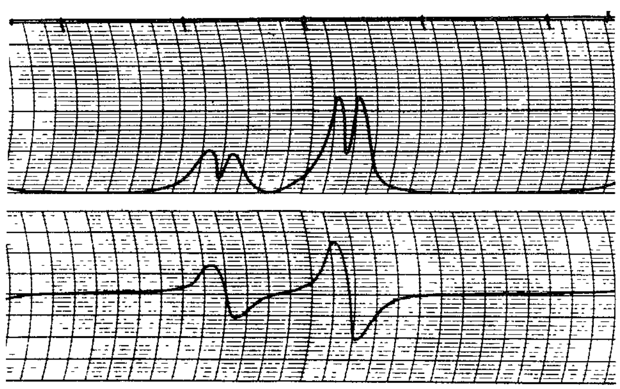

Fig. 5 - Data sample.