A N.M.R. SPECTROMETER FOR KNIGHT SHIFT INVESTIGATIONS

by

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ABSTRACT

This thesis describes the design, assembly, operation and behaviour of a nuclear magnetic resonance spectrometer of the Pound-Knight type built for investigation of Knight shift in metals and alloys.

A brief introduction to nuclear magnetic resonance is given followed by a short discussion of the Knight shift. A short description of the various arrangements for observing nuclear magnetic resonance is given and after pointing out the requirements for observing the Knight shift in metals, our choice of the spectrometer is justified. The working of the spectrometer as a whole unit is explained and this is followed by a description of its various components. The technique of determining frequency is described in detail by giving a typical example of Al27 signal from a solution of $AlCl_3$.

The behaviour of the spectrometer is discussed and its use in detection of various signals is given. The necessary conditions for obtaining good signals are summarised. The temperature variation and also the homogeneity of the magnetic field are studied with the aid of the spectrometer. The accuracy and usefulness of the equipment is tested by measuring the Knight shift in aluminium metal.

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CHAPTER 1

General Considerations on the Knight Shift

INTRODUCTION

Nuclear Magnetic Resonance (n.m.r.) results from the interaction of electromagnetic radiation with a system of atomic nuclei placed in a magnetic field. It is detected by the absorption or induction of a signal at radiofrequency. This phenomenon is basically well understood (see below) and it has given rise to a vast new branch of spectroscopy.

Not only does it yield information on nuclear properties but because it is very sensitive to the environment of the nucleus it gives information on the internal electric and magnetic field in matter.

The nuclear properties investigated by n.m.r. are the magnetic moment and the angular momentum or spin of the nucleus. Also it gives information on the nuclear quadrupole coupling constant which is the product of the electric quadrupole moment of the nucleus and the electric field gradient at the site of the nucleus.

The chemists make ample use of n.m.r. techniques in the determination of the structure of some molecules. It is particularly well adapted for the study of hydrogen, an element which often escapes detection by X'ray techniques.

The n.m.r. condition has been found in matter in all its forms. To the physicists interested in the study of solid state it gives information on relaxation mechanisms as well as on electric and magnetic fields in bulk matter.

Since the discovery by Knight in 1949 of the metallic shift or Knight shift, physicists have taken a renewed interest in its techniques as this shift is quite closely related to the transport properties of metals.

The present work deals with the construction and the study of the behaviour of a n.m.r. spectrometer for the investigation of the metallic shift in metal alloys and we will review in this introduction only those aspects of the theory and techniques of n.m.r. that are relevant to the understanding of this thesis. For more general discussions we refer the reader to the great wealth of excellent literature on the subject e.g. Andrews (1956), Pake (1956) and Bloembergen, Purcell and Pound (1948).

1. The Nuclear Magnetic Resonance Condition

Let us suppose that a nucleus has a magnetic moment $\vec{\mu}$ and an angular momentum or spin I. These two properties are related to each other as follows

$$\vec{\mu} = g\frac{e\hbar}{2Mc}\vec{I} = \gamma\beta\vec{I} \qquad (1)$$

where $\beta = \frac{e\hbar}{2Mc}$ is by analogy with the electronic case called the Nuclear magneton, $\hbar$ is the Planck constant divided by 2π, M and e are the mass and charge of the proton respectively and c the velocity of light. Finally g is a proportionality factor characteristic of the nuclear isotope and its state. The values of g cannot be derived in theory but are determined by experiment. They are referred to as nuclear g-factor.

The energy U of this nucleus in a magnetic field H_0 is

$$U = -\vec{\mu}\cdot\vec{H}_0 = -g\frac{e\hbar}{2Mc}\vec{I}\cdot\vec{H}_0 \qquad (2)$$

$$= -g\beta m H_0 \qquad (3)$$

where m is the magnetic quantum number which can have (2I + 1) values; I, I - 1, •••, -I + 1, -I. Hence the nucleus has 2I + 1 distinct energy levels due to its interaction with the magnetic field. These levels are equally spaced with a separation of $g\beta H_0$ between successive levels. The selection rule governing transitions between these energy levels is the same as for Zeeman effect. Transitions are allowed for which $\Delta m = \pm 1$. A quantum of energy can excite transitions between the levels if it has the same magnitude as the level spacing

$$h\nu_0 = g\beta H_0 \qquad (4)$$

which is the resonance condition. ν_0 is the resonance frequency.

This resonance condition can also be arrived at by semi-classical considerations (see for instance Pake 1950). It is seen then that the resonance frequency is the same as the Larmor precession frequency of a nuclear dipole of moment $\vec{\mu}$ in a steady magnetic field H_o.

To observe this resonance, the sample containing the the nuclei to be investigated is placed in the gap of a magnet supplying a large steady magnetic field H_o. At right angle to the direction of H_o, a radio-frequency coil surrounding the sample supplies a small oscillating magnetic field H_1 cos $(2\pi\nu t)$. When the resonance condition is obtained, i.e. when $\nu = \nu_o = \frac{g\beta H_o}{h}$, transitions occur between adjacent nuclear levels and one observes either absorption of the radio-frequency energy supplied to the coil (**n.m.r.** absorption of Bloembergen, Purcell and Pound 1948) or the e.m.f. induced in a coil placed at right angle to both the steady field H_o and the r.f. field H_1 cos $(2\pi\nu t)$ (nuclear induction of Bloch, Hansen and Packard 1946). The resonance condition is reached either by varying the magnetic field H leaving ν_o at fixed value or changing ν in a constant fixed H_o.

In the semi-classical treatment, one considers that the linearly oscillating r.f. field can be decomposed into two circularly polarised components rotating at the angular frequency $w = 2\pi\nu$ in opposite directions. Resonance occurs when one of these circularly polarised components rotates at the same angular frequency and sense as the nuclear dipoles precessing at the Larmor precession frequency.

In the foregoing treatment we have assumed that each nucleus was isolated and similarly located in the magnetic field. We now have to consider what happens to an assembly of weakly interacting nuclei to get a more complete picture of the n.m.r. phenomenon. These weakly interacting nuclei will be distributed among the possible energy levels according to the Boltzmann distribution law and their relative population N(m) will vary with temperature T according to $N(m) = Ae^{-g\beta mH_0/kT}$ where A is a constant. Thus the lower levels will be more densely populated than the higher ones.

Let us consider for instance an assembly of nuclei with spin I = 1/2 at room temperature. In a field H_0 each nucleus has two possible energy levels: $\pm \frac{g\beta H_0}{2}$, the lower level being slightly more populated than the higher one. Upon the application of a r.f. field at resonance, two things will happen. Some transitions will occur raising nuclei from lower to higher level (absorption) while some transitions will occur lowering nuclei from higher to lower (induced emission). Since we can neglect here spontaneous emission and since the probabilities for absorption and induced emission are almost equal, the net absorption of energy would last only as long as the population of the lowest level is greater than that of the highest. As the population would soon be equalised if there were no means by which the nuclei can relax to the lowest state apart than emission induced by the r.f., the phenomenon would very soon be saturated, and would be only a transient phenomenon of very short duration. When trying to observe the resonance, the signal would rapidly decay during the time of observation. However, this is not the case. We were led to this state of affair because we have neglected the presence of the lattice in thermal agitation. The nuclei can exchange quanta of energy with the lattice, (which will warm up) and relax to the ground state independently of the r.f. field, and maintain the Boltzman distribution corresponding almost to the temperature of the bulk sample (at least as long as the r.f. field is not too large). This phenomenon is known as the spin lattice relaxation, and it is characterized by T_1, the spin-lattice relaxation time. T_1 is related to inverse of the transition probability for lattice induced emission. It is approximately the time it takes for the system disturbed from equilibrium to come back to equilibrium by lattice induced emission. This process thus makes a net absorption of r.f. energy possible.

2. The n.m.r. Spectrum; Line Width and Line Shape

We have assumed up to this point that the assembly of the nuclei is weakly interacting and we have neglected to give the consequences of this weak interaction on the absorption phenomenon. We will see presently that when we take this interaction into consideration, it leads to an absorption line of a definite non zero width.

The interaction between nuclei is due to the presence of the magnetic dipole moment associated with the spin. Each nuclear dipole finds itself not only in the applied field H_o, but also in a small additive local magnetic field produced by the neighbouring nuclear dipoles. The direction and magnitude of the local field differs from nucleus to nucleus, depending on the magnetic states of the neighbours. The magnitude of the local field is of the order of μ^2/r^3, where r is the internuclear distance. We thus expect that the resonance condition varies from nucleus to nucleus by this amount. The resonance line is broadened by an amount $\Delta\nu \sim g\beta H_{local}$ around the center frequency ν_o.

The problem of evaluating the width of the line and predicting its exact shape is a difficult one. Bloch (1946) has derived a phenomenological theory of the complex susceptibility of such an assembly of classical dipoles and predicted a line of Lorentz shape and of width at half maximum $\Delta\nu = \frac{1}{\pi T_2}$ where T_2 is the spin-spin relaxation time. T_2 is, roughly speaking, the time for the system of spin to attain equilibrium with itself and depends on the dipole-dipole interaction discussed above.

Van Vleck (1948) using quantum theory has studied in detail the effect of dipole-dipole interaction. Even if his calculation did not yield the shape of the line, he was able to find exact expression for the second and fourth moment of the line. These expressions involve the nuclear magnetic moment and the spatial co-ordinates of the dipoles. He solved this problem for the case of single crystals and for the case of polycrystalline samples. The second and fourth moment obtained generally fit a Gaussian curve.

In liquids, the resonance line is narrower than in solids since the reorientation and the diffusion of molecules is usually so rapid that the local magnetic field is smoothed out to a very small average value, yielding quite a narrow line. The theory of the width of line in liquids is discussed by Bloembergen, Purcell and Pound (1948).

The line width in metal and metal alloys presents some special features which we shall discuss later when we discuss the metallic shift.

3. The Metallic or Knight Shift

It was first observed by Knight (1949) that the n.m.r. signal from metallic copper occurred at a higher frequency than that from copper in a non metallic form (e.g. CuCl) in the same external field. Afterwards a shift of the same nature was observed in the case of many other metal nuclei. These shifts in frequency were found to be larger by about an order of magnitude than any of the known chemical shift which arise when the same nuclear species is observed in different compounds. The mechanisms responsible for the chemical shift seem to be incapable of explaining the large shifts in metals. The shift in metals is often referred to as Knight shift.

3.1. General Expressions for the Shift

Townes, Herring and Knight (1950) gave an explanation of this effect. The shift is essentially due to an extra energy interaction in the metal between the nucleus and the conduction electrons. When this extra term is added to equation (2) that describes the energy of interaction of a nucleus in the magnetic field H_o, it is found that, to the first order of perturbation, the energy levels are now given by

$$U(m) = -g\beta H_o\left(1 + \frac{\Delta H}{H_o}\right) \qquad (5)$$

instead of equation (3), where $\Delta H/H_o$ can be written as

$$\frac{\Delta H}{H_o} = \frac{8\pi}{3}\chi_p M\langle|\Psi_F(0)|^2\rangle_{Av} \qquad (6)$$

Here χ_p is the Pauli spin susceptibility per unit mass and M the mass of the atom, and $\langle|\Psi_F(0)|^2\rangle_{Av}$ is some suitabble average of the probability density at the nucleus of the conduction electrons having energies near the Fermi limit.

Then from equation (5) and the selection rule we get the following resonance condition in case of a metal

$$h\nu_{metal} = g\beta H_0\left(1 + \frac{\Delta H}{H_0}\right) \qquad (7)$$

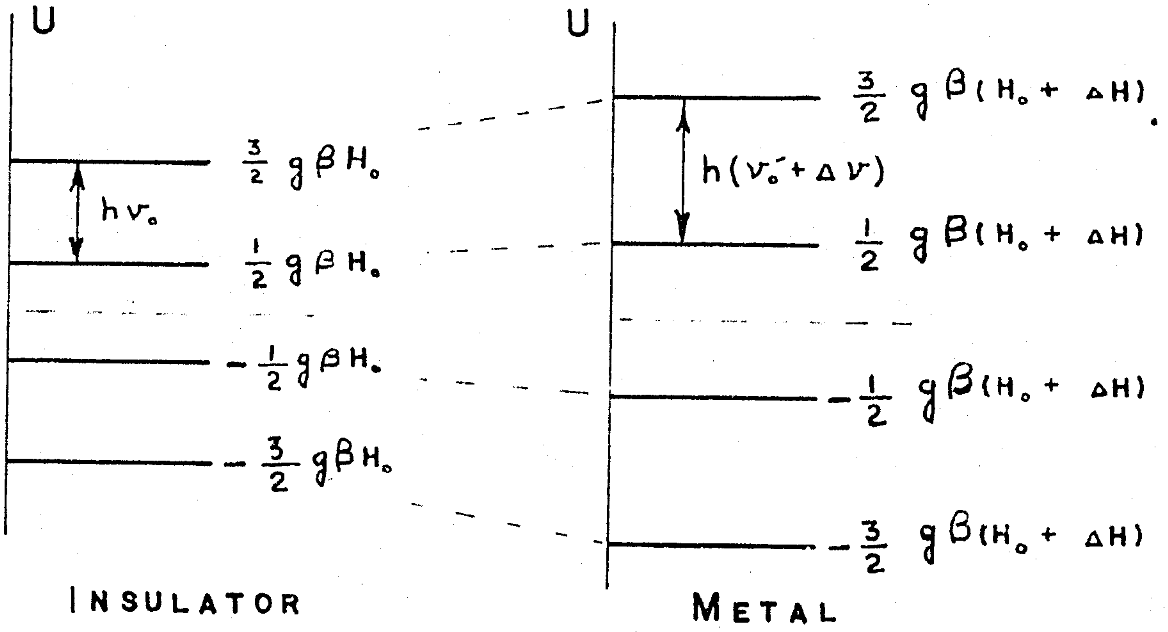
and

$$\nu_{metal} = \nu_0 + \Delta\nu \qquad (8)$$

whence

$$\frac{\Delta\nu}{\nu_0} = \frac{\Delta H}{H_0}$$

For a nucleus of spin 3/2, the energy levels in an insulating material and in the metal are sketched below



In this sketch $\Delta\nu$ is exaggerated to show clearly the result of the interaction of the nuclei with the conduction electrons in metals. In fact the $\frac{\Delta\nu}{\nu_0}$'s observed range between approximately 0.000 for Be9 to 0.025 for Hg199.

$\Delta\nu$ is a quantity that in principle can be measured easily. Indeed it is sufficient to place in a given constant field H_o the metal to obtain ν_{metal} and then the same metal nuclei in form of a salt in solution, or in solid form, to obtain ν_o. $\Delta\nu$ is then the difference between the two. The $\Delta\nu$ so obtained is then that which is due to the interaction of the nucleus with the unbalanced spins in the conduction band, in so far as ν_o is exactly the resonance frequency for a free spin. However, because of the presence of a chemical shift the value of ν_o so obtained is not that of a free spin and a correction must be made for the chemical shift before the $\Delta\nu$ predicted by equation (6) is obtained.

All the shifts observed in the various metal isotopes have been towards higher frequency. In all cases these shifts have also been found proportional to H_o, the applied external field and hence $\frac{\Delta\nu}{\nu_0} = \frac{\Delta H}{H_o}$ found constant.

The effect of temperature on the shift is small for the metal nuclei where this dependence has been studied namely, the alkali and Ga. It is related to the change of atomic volume and this dependence as well as the dependence of the shift on pressure awaits further investigations.

We may now ask the question as to what knowledge is gained from a measurement of $\Delta\nu$. As seen from equation (6), $\Delta\nu$ is proportional to the product of two quantities χ_p and $\langle |\psi_F(0)|^2 \rangle_{Av}$ which unfortunately cannot be measured separately in most cases. A knowledge of this product can nevertheless help in a better understanding of the theory of metals. Since it is often possible to get a fairly reliable estimate of either of the two unknowns, we can compare the value obtained from the other to the theoretical prediction of various models.

The problem of evaluating $\langle |\psi_F(0)|^2 \rangle_{Av}$ is rather difficult and in all cases except the simplest our knowledge of its value is insufficient. It is one of the fundamental problems of the theory of metals and any measurement where this quantity appears is of interest.

To get a good value for χ_p is also difficult. The usual expression for χ_p based on the free electron model of a metal does not give too good agreement but for the simplest cases. To get a better value a detailed knowledge of electronic structure of the individual metal is essential. Both these problems are discussed in more detail by Knight (1956).

3.2 On the Line Width and the Relaxation Time in Metal

The problem of evaluating the line width and the spin-lattice relaxation time is discussed by Bloembergen and Rowland (1953). We shall only quote the main features briefly.

The fundamental process involved in the spin lattice relaxation time T_1 is the following. The exchange of energy between the nuclear spin system and the electron system occurs when the two spins, nuclear and electronic, flip simultaneously. The quanta of energy involved are not the same and the difference of energy which can be written as $\pm \hbar(g_e \mu_B - g\beta) H_o$ appears in form of a change of momentum of the conduction electrons. As only the electrons near the Fermi level can take such small amount of energy, we expect that T_1 will be closely related to the Knight shift which also depends on the electron near the Fermi limit. Indeed it is found that

$$T_1 \left(\frac{\Delta H}{H}\right)^2 = \frac{\hbar}{\pi k T} \left(\frac{\mu_B}{g\beta}\right)^2 \qquad (17)$$

This expression is found to hold only approximately and a better expression is obtained when the interaction of the nuclear spin with the other than the s part of the wave function of the electron is taken into account.

The width of a metal n.m.r. line is governed by the nuclear dipolar interaction (Van Vleck dipole-dipole interaction) and also by the finite life time T_1, the spin lattice relaxation time. At low temperatures the first process is more important whereas the second predominates at high temperatures. Finally if the nucleus investigated has a non-zero electric quadrupole moment and is placed in a non-cubic field gradient, the line may be broadened considerably by this interaction.

The presence of magnetic impurities i.e. of transition element in a metal is also an important factor in the broadening of the line.

In the rest of this thesis we have given a detailed description of the Pound-Knight spectrometer which has been built to study Knight shift and line width in metals and alloys. The working of each component of the spectrometer is explained in considerable details. The behaviour of the spectrometer has been thoroughly studied in case of Al27. It is hoped that this spectrometer can be put to successful use for investigation of Knight shift and line width for dilute alloys such as Al-Mn and Al-Fe as a probe to the effect of magnetic impurities in metals. As explained in Section 5 of Chapter II, the order of accuracy required for such an investigation is approximately 1 part per million. With our frequency measuring system we have been able to achieve this accuracy.

CHAPTER II

DESCRIPTION OF THE SPECTROMETER

1. A Brief Survey of the Various Arrangements in Use To-day

There are essentially two different methods that have been used in the detection of the nuclear magnetic resonance phenomenon. These are

(1) the method of nuclear resonance absorption due to Bloembergen, Purcell and Pound. (Usually abbreviated as BPP)

(2) the method of nuclear induction due to Bloch, Hansen and Packard (usually abbreviated as BHP).

In the method of nuclear resonance absorption, the sample in the magnetic field is placed inside a radio frequency coil and the resonance effects are detected by their reaction on the circuit supplying the radio frequency field whereas in the induction method two r.f. coils are used, one connected to a transmitter and a second at right angle to it picks up the nuclear resonance effect and is connected to a receiver.

We will first describe briefly the various spectrometers based on the method of detection of BPP. Many workers have designed circuits for this type of detection and we will describe the essential features of each circuit.

1.1. The Bridge Arrangement of BPP

Purcell, Torey and Pound (1946) set up the first successful nuclear magnetic resonance absorption experiment. They used a bridge arrangement which was modified by BPP (1948).

The principle of the method is rather simple. Two almost identical tuned circuits are connected in parallel to a signal generator. The coil of one circuit contains the sample under investigation and is placed between the poles of the magnet. The dummy circuit in the other branch is essentially the same but is not located in the field.

An additional electrical half-wave-length of cable is placed in one circuit and this enables to subtract the output of two circuits and feed it into an amplifier. If the two circuits were identical and the length of cable exactly half-wave-length the signal from the dummy circuit would exactly cancel that from the circuit containing the sample when the frequency is off resonance.

When searching for resonance, the bridge is never completely balanced but is unbalanced to such a degree that the voltage appearing at the point where the two circuits join is large compared to the change in this voltage by nuclear absorption or dispersion.

The advantages of the bridge are (1) reduction of the r.f. level at the input to the amplifier to permit considerable r.f. amplification before detection, and (2) the reduction in the relative magnitude of output fluctuations in the signal supplied by the signal generator.

This method is a very versatile arrangement for resonance measurements on materials of all kinds but it is not very convenient when the object is to search slowly for unknown lines because the bridge must be kept continually in adjustment. In such cases the marginal oscillator method is preferred.

1.2. Marginal Oscillator Method

The specimen is contained in a cylindrical coil which is placed perpendicular to the direction of the steady magnetic field. This coil and a condenser form a tuned LC circuit in the grid circuit of a r.f. oscillator. The oscillator may formally be regarded as placing a negative resistance in parallel with the tuned circuit. Oscillations are sustained if this negative resistance compensates the positive shunt resistance of the circuit. Radio frequency current flows in the specimen coil and the absorption of energy occurs when the resonance condition is reached. In effect, the positive shunt resistance is decreased, and the oscillation amplitude falls every time the modulated 'steady' magnetic field passes through the resonance line.

The audio-modulated r.f. voltage appearing across the coil may be either rectified within the oscillator itself or it can be further amplified and then rectified. The former is done in an oscillator detector circuit. Hopkins (1949) has used this type of circuit. Only audio-amplification is needed before displaying the signal.

Circuits have been developed by Pound (1947) and Pound and Knight (1950) based on the second choice of amplifying at radio frequency before rectification (see Section 3 for details of a Pound and Knight spectrometer). It leads to an improved signal-to-noise ratio, the noise factor is almost the same as obtained in bridge method.

The instrument is useful when the object is to discover the resonance line whose gyromagnetic ratio is only roughly known. The line is slowly searched by varying the magnetic field at fixed r.f. or varying the frequency at fixed field.

The marginal oscillator methods have a great advantage as compared to bridge methods. They give a pure absorption signal proportional to χ''. The dispersive component of the susceptibility produces a frequency modulation of the oscillator to which the rectifier does not respond.

In these methods the level of the oscillation is kept low to achieve maximum sensitivity. Also, at higher levels the noise factor is increased. But the main reason for keeping the level low is to prevent the saturation of the specimen. The r.f. amplitude across the specimen coil cannot be reduced much below 0.1 V to get a stable operation of the oscillator. Many solids would be saturated at this level. For solids having a long spin-lattice relaxation time, it often becomes necessary to work with a r.f. level of few millivolts to avoid saturation. The marginal oscillator methods cannot be applied to such cases and in this respect they are limited in their application.

1.3. Super-Regenerative Methods

A super-regenerative oscillator is characterized by the repeated build up and decay of its oscillations. The circuit is made alternatively oscillating and non-oscillating by the application of a periodic voltage from a separate oscillator to one of the electrodes of the oscillator tube. The source of this periodic voltage is a separate oscillator called the quench oscillator.

As in the marginal oscillator method, the sample to be investigated is placed in the coil which forms the tuned LC circuit with a variable condenser. The oscillator tube effectively places a negative resistance with the tuned circuit. The negative resistance is inversely proportional to its mutual conductance. During the 'on' and 'off' periods the mutual conductance is rendered high or low thus helping in building or decaying of the oscillations.

The Quench frequency and the circuit constants are adjusted so that the oscillations build up exponentially from the level of any voltage of the correct frequency developed across the circuit.

During and just after each 'on' period, the specimen is subjected to a r.f. field. Two effects may occur if the coil is oriented correctly in the steady magnetic field, which is adjusted to the resonance condition. First, the absorption of energy by the nuclei produces a reduction in the integrated pulse energy. Secondly, if the period of the quench oscillator is not long compared with T_2, the integrated pulse energy is increased. In general, the resonance condition causes a change of the integrated pulse energy which may be detected either by grid rectification in the oscillator or by reception in a receiver tuned to the proper radio frequency.

This method was introduced by Roberts (1947) for the measurement of nuclear magnetic moments. Circuits have been described by Soutif (1951) and Gutowsky, Meyer and McClure (1953).

The response in the super-regenerative method is very complicated and makes it unsuitable for general experiments on nuclear magnetic resonance. It is commonly used in experiments for the determination of nuclear magnetic moments. The signal-to-noise ratio obtained with this method is quite good.

1.4. Nuclear Induction Methods

In the nuclear induction experiments two coils are used. One is a transmitting coil and the other is a receiving coil. Sometimes a combined transmitting and receiving coil is used. Bloch, Hansen and Packard (1946 a,b) devised a double-coil nuclear induction method which was used in their discovery of n.m.r. phenomenon.

The signal is received in the second coil placed with its axis perpendicular both to the steady field and to the axis of the transmitter coil. With a perfect geometric arrangement it is possible to get the signal in the receiving coil only due to the precession of the resultant magnetic moment of the nuclei. This signal may be amplified before rectification.

The specimen is placed within the receiving coil between the poles of a magnet. The transmitting coil, with its axis in the third mutually perpendicular direction is supplied with current from a signal generator and is wound outside the receiving coil. The receiving coil is tuned by a parallel condenser and forms the input circuit of the first stage of a r.f. amplifier. The method of displaying the signal is the same as with the bridge arrangement. The only essential difference between this and the bridge arrangement lies in the r.f. circuit.

The nuclear induction methods have got certain advantage over the nuclear resonance methods as they can give information about the sign of nuclear magnetic moment and the dispersive component of the signal.

There is not much choice between the single and double-coil methods of observing n.m.r. For work at low temperatures simplicity within the cryostat is desired. The single-coil methods are preferable in such cases.

In the nuclear induction method the r.f. level can be varied over a much wider range than in the marginal oscillator method and this represents an advantage as mentioned before.

2. A Discussion of our Requirements

As mentioned in Section 5 of Chapter I, we wanted a spectrometer to investigate the variation of the Knight shift and to study the line shape and line width of the n.m.r. spectra in Al-Mn system as a probe for the effects of the magnetic impurities in pure metals. Eventually these measurements will also be carried out at low temperatures.

Experiments at low temperatures require that the arrangement within the cryostat be simple and this point of view had to be taken into consideration when choosing among different methods. We preferred single coil methods for nuclear absorption to nuclear induction methods as the latter require quite a complicated set up within the cryostat. The single coil methods require only one coil linked to the oscillator by a single coaxial cable.

In the single coil methods we could choose among the bridge arrangement of BPP, marginal oscillator method and super-regenerative methods. While making a brief survey of the various arrangements in section 1 of this Chapter we mentioned that the response in the super-regenerative methods is difficult to interpret and because of that we have rejected it. We were thus left to choose between the bridge arrangement of BPP and marginal oscillator method.

The bridge arrangement has the drawback that it has to be kept continually in adjustment and also it gives a mixture of absorption and dispersion signals unless carefully adjusted. We thus decided in favour of building a spectrometer based on marginal oscillator method which as mentioned earlier gives a pure absorption signal.

We have a permanent magnet giving a field of about 7 kg (see Section 6). So, the choice of the type of spectrometer was restricted to one which operates with a varying frequency and a constant magnetic field. Any device for the study of nuclear resonance effects in solids should be so designed that the optimum signal-to-noise ratio is nearly achieved. For the measurement of the shift, an experimental arrangement which plots the derivative of absorption is best for determining exactly the center of the line. Taking all these factors into account it appeared that the spectrometer described by Pound and Knight (1950) would be the most suitable. In fact our spectrometer is quite similar to that described in Teeters (1955). His work is a study on the Knight shift in alloys and his spectrometer was found to be exactly what we needed.

3. Description of the Spectrometer (Pound-Knight type)

The working of the spectrometer is best understood by considering the block diagram in Fig. 1. The sample is contained in a cylindrical coil placed in the field of the permanent magnet with its axis perpendicular to the direction of the field. It is connected by a coaxial cable with a variable condenser in the oscillator detector box forming a tank circuit. The steady magnetic field of the magnet is modulated at a low audio frequency (74 c/s) by means of

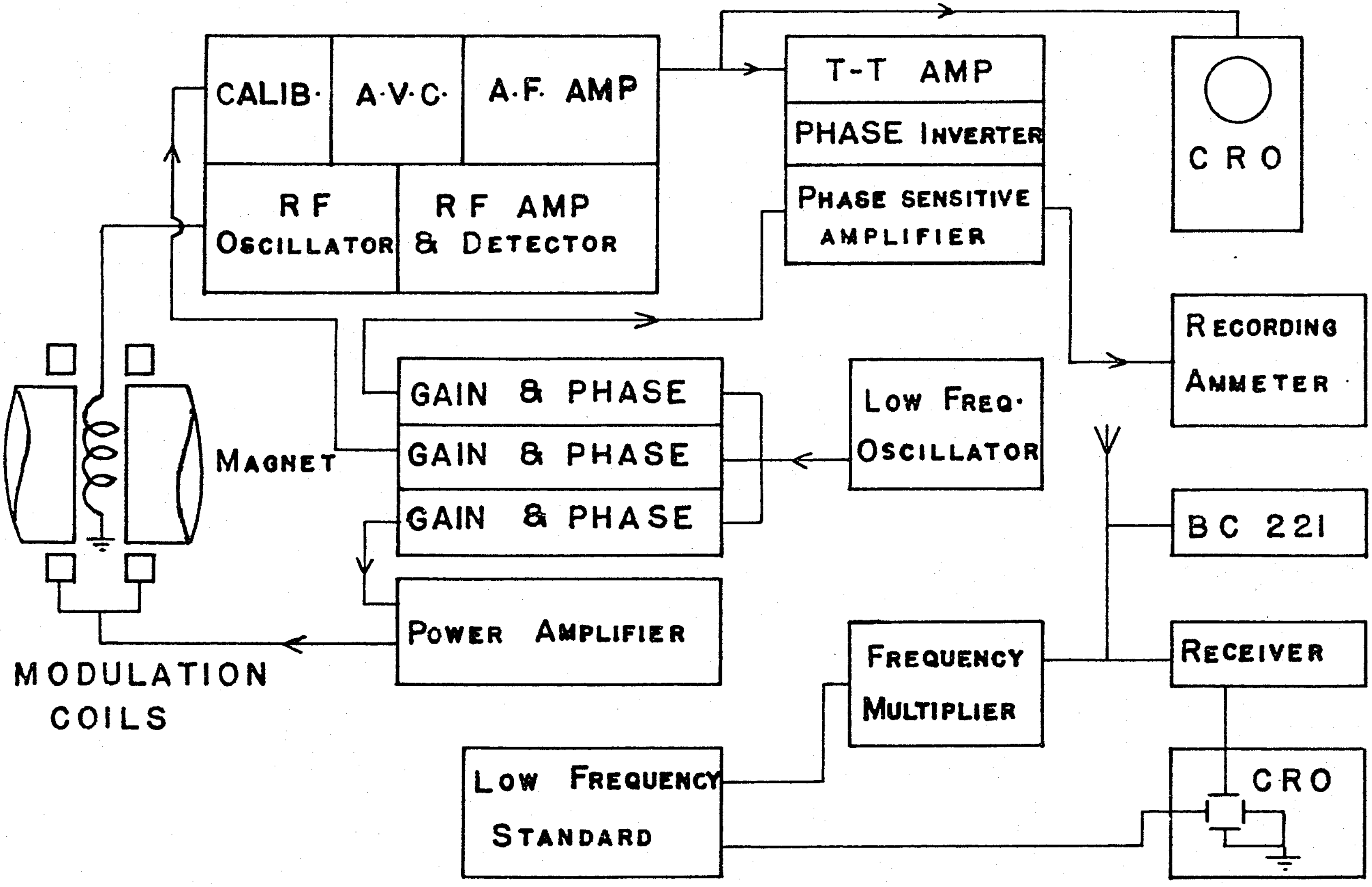


FIGURE I - BLOCK DIAGRAM OF THE NMR SPECTROMETER a pair of coils attached to the pole faces of the magnet.

The resonance condition is obtained by sweeping slowly in frequency and this in turn is obtained by driving slowly with a synchronous motor the variable condenser in the tuned circuit.

In the oscillator detector, the r.f. oscillation is first amplified by two or four stages of the r.f. amplifier. When the resonance condition is obtained the r.f. carrier is audio modulated and this is demodulated in the detector. The detected signal then goes through an audio preamplifier before leaving the oscillator detector box. Also included in this circuit is an automatic volume control (A.V.C.) whose role is to keep the level of r.f. oscillation constant over long periods of time and stop the oscillation amplitude from changing as the frequency is changed.

The audio signal coming out of the preamplifier can be observed directly on a C.R.O. or after passage through the Phase Sensitive Detector (P.S.D.) recorded on a chart. These two methods of detection of the signal are often called wide and narrow band detection respectively.

In the first method the absorption signal is displayed on the oscilloscope. The field is modulated with an amplitude several times the width of the absorption line. The signal from the audio amplifier is sent to the vertical plates of the C.R.O., the time base of which runs in synchronism with modulation. The oscillograph trace then gives an indication of the absorption line.

For weak resonance lines the P.S.D. method is used. The modulation amplitude is cut down to a fraction of the anticipated line width. As the resonance is passed through by the changing frequency of the oscillator, the level of oscillation varies coherently with the modulation in a phase that reverses at the center of the line. The tuned audio amplifier and P.S.D., fed also directly with the modulation frequency, produce a d.c. output which is proportional to the first derivative of the absorption line, which is then recorded on the chart.

The audio frequency originates from a low frequency oscillator whose signal is sent to a distribution box comprising the three units shown in the block diagram as Gain and Phase. The role of each unit is to give out an audio signal of the proper amplitude and phase. One of them feeds the P.S.D. A second is used for the calibration of the oscillator detector (not used to date) or else to drive the horizontal plates of the C.R.O. A third one serves to drive the modulation coils after proper amplification through a power amplifier.

Finally in the block diagram shown in Fig. 1 we can see the various elements of the frequency meters. First a B.C. 221, which is a frequency meter unit developed by the Army and is capable of an accuracy of a few hundredths of 1%. This unit works independently.

The other elements form a unit capable of muuh higher accuracy. The principle involved is the following, a signal at 10 kc/s from a low frequency standard of high stability is multiplied a few hundred times and mixed in a communication receiver with the signal emitted by the spectrometer. The beat frequency between the r.f. signal and proper harmonic is displayed on a C.R.O. whose time base is driven directly at 1 kc/s or 100 c/s by the original low frequency standard. Lissajous figures are obtained on the screen of the C.R.O. which permit the identification of the frequency every 100 c/s. With this method explained in more details in Section 5 of this Chapter, an accuracy of about 1 part per million is possible.

3.1. The Oscillator Detector

The circuit diagram of the oscillator detector is given in Fig. 2. All this circuit was mounted in a brass box 10" x 12" x 4", with very rigid walls to avoid microphonics and to insure rigidity of the component parts. Also in this box, there are particular walls to isolate the various circuits. In one of these there is the oscillator circuit

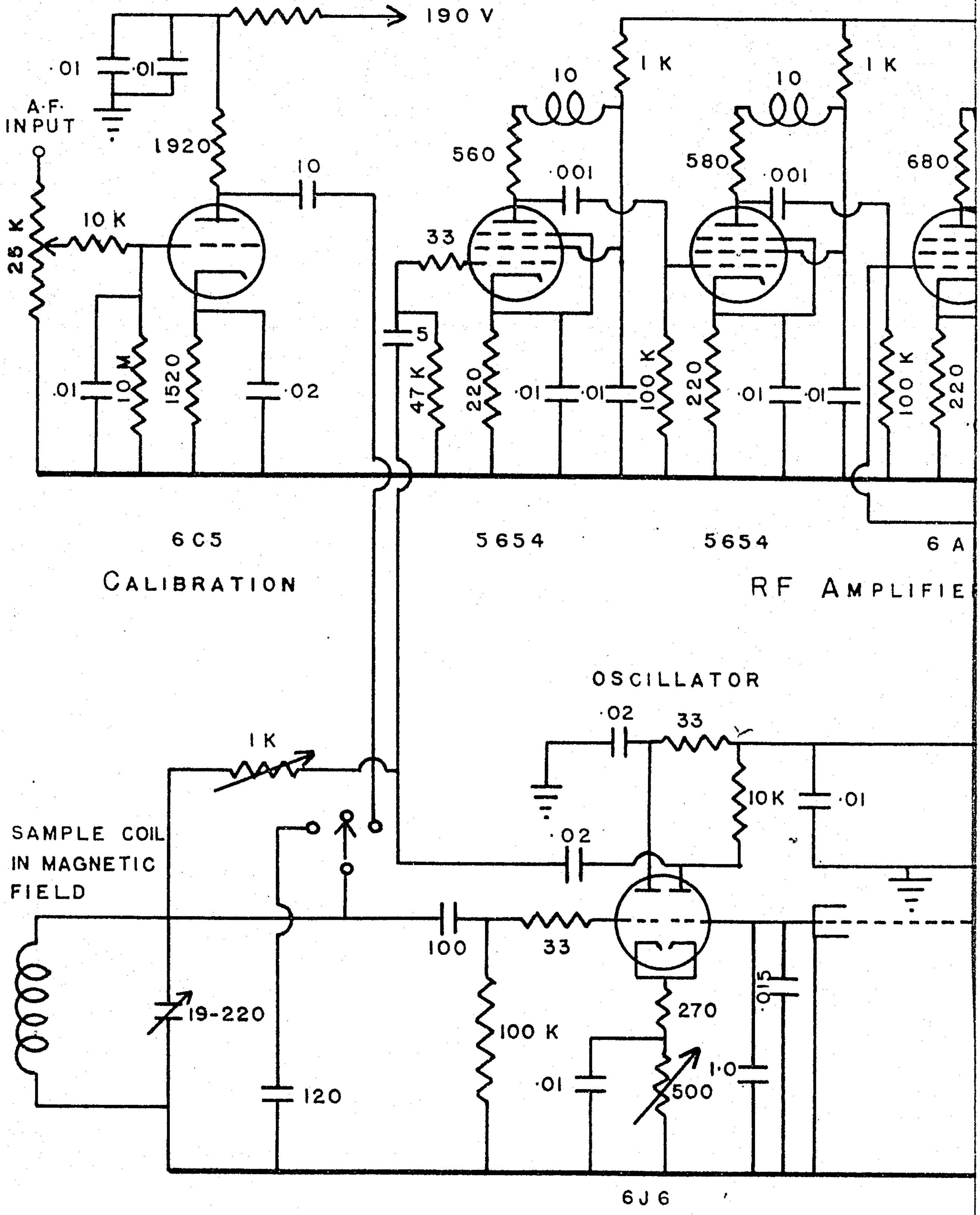
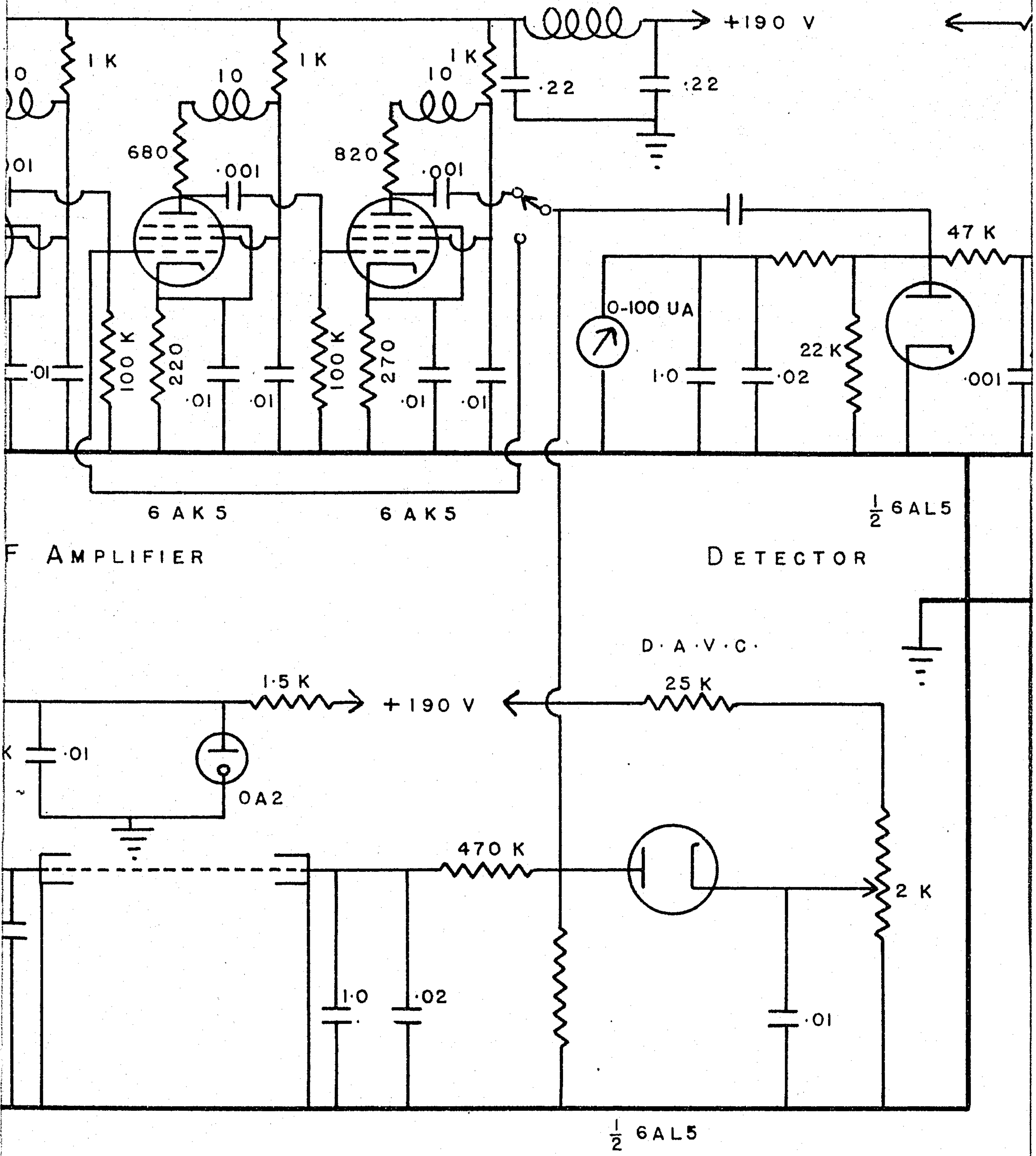
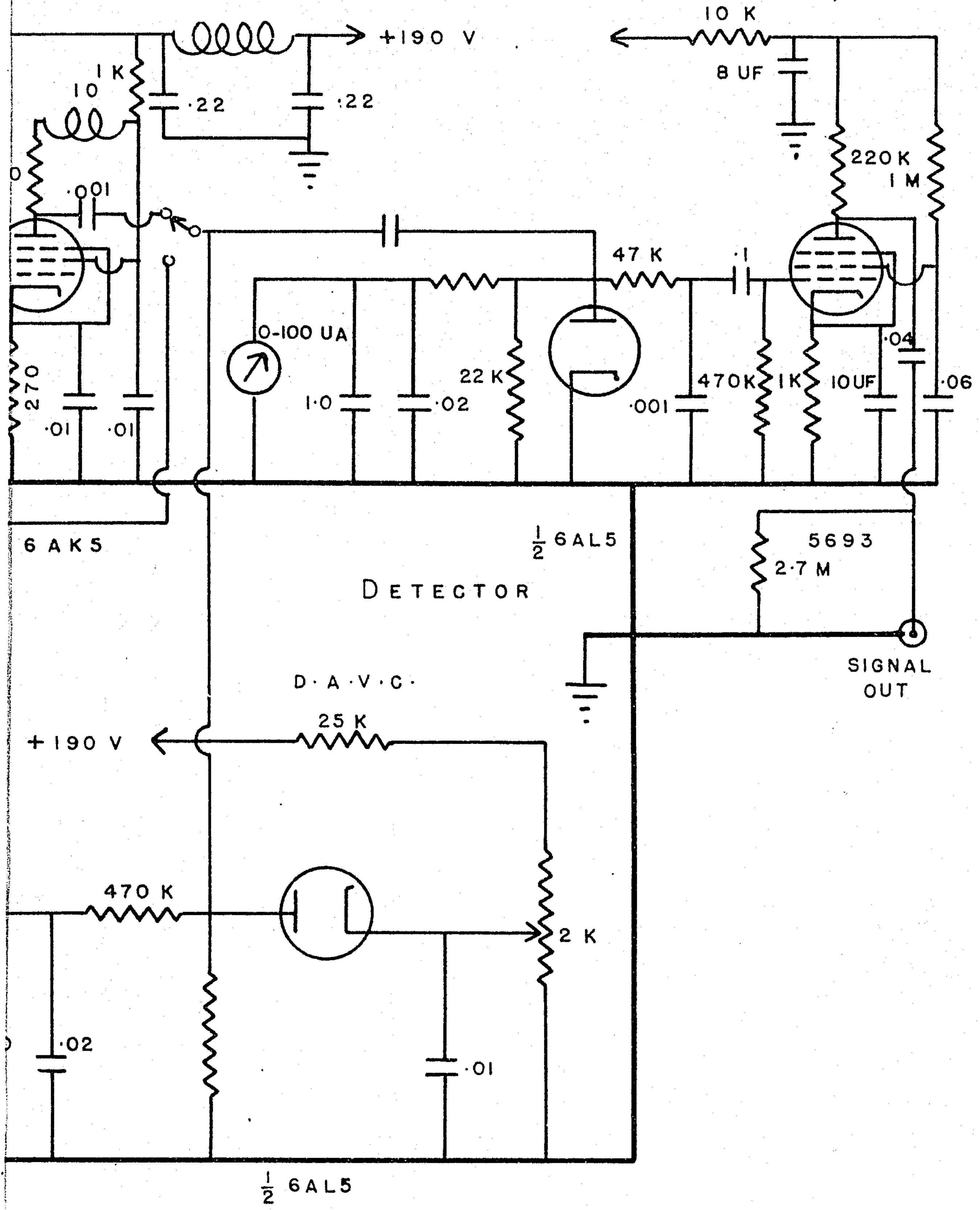


FIG. 2 — CIRCUIT DIAGRAM OF THE OSCILLATOR DET



LATOR DETECTOR·



+190 V
10 K
8 UF
1 K
10
·22
:22
·001
220 K
1 M
47 K
·1
0-100 UA
270
·01
·01
1·0
·02
22 K
·001
470K
1K
10UF
·04
·06
6 AK5
½ 6AL5
5693
2·7 M
DETECTOR
SIGNAL
OUT
D·A·V·C·
+190 V
25 K
470 K
2 K
·02
·01
½ 6AL5

with the variable condenser of the resonant tank circuit. This is a Cardwell straight line frequency variable air condenser (19-220 $\mu\mu F$) which already includes a demultiplication worm and gear arrangement. To drive this condenser and sweep over frequency, a motor is mounted directly on the brass box with a second worm and gear arrangement attached to the brass box.

The sample coil that goes in between the pole pieces of the magnet below is held at the end of a rigid coaxial line made of a central copper wire and a hollow brass cylinder 1/2" o.d. This coaxial line can be attached directly into the brass box by an amphenol connector.

The component parts of the oscillator-detector can be seen on Fig. 2 and they are; an r.f. oscillator, two two stage r.f. amplifier, a detector or demodulator, an audio preamplifier, a calibrator and an automatic volume control for the oscillator.

The principle of operation of the oscillator has been discussed by Pound and Knight (1950). We will explain it briefly. As mentioned earlier, the coil and the variable condenser form a shunt resonant circuit. The r.f. signal is supplied to this circuit by connecting it to an electronic circuit that forms a two terminal negative resistance and thus sustains oscillations in the resonating circuit. To just sustain oscillation the magnitude of the negative resistance must be just equal to the positive shunt resistance of the tuned circuit. The level of oscillation is sensitive to the small changes in shunt resistance resulting from passing through nuclear resonance. Such variations in level are observed as variations in the amplified r.f. voltage after rectification.

A 6J6 twin triode is used for the oscillator itself, and the signal from the tank circuit is amplified by a two stage r.f. amplifier and can be further amplified by another similar two stage amplifier at will. Afterwards the signal is detected and the envelope of the amplitude modulated r.f. carrier is amplified by a one stage audio amplifier or preamplifier before becoming available for display. A simple automatic volume control is incorporated in the circuit to keep the level of oscillation constant with a time constant which is large compared to the time necessary to go through the resonance signal.

The amplitude of the oscillator can be evaluated by a microammeter which reads a current proportional to the r.m.s. of the r.f. after amplification. Finally this level of oscillation can be adjusted over a large range of value by varying the cathode bias of the 6J6 and the 1K potentiometer in the feedback circuit of the oscillator.

In this circuit there is also a calibrator which is an amplifier that can feed to the oscillator an audio frequency at modulation frequency. That audio signal is superposed on the r.f. carrier before r.f. amplification. It permits a calibration of the amplitude of the n.m.r. signal. It has not been used in the past but will be useful in comparing the amplitude of various n.m.r. signals.

We would like before closing this section to make the following comments of practical interest. The electric motor is fixed on the side of the box and is connected by a brass axle to a worm gear which drives a spur gear attached to the shaft of the condenser. It was observed during a series of experiments that the proper matching of these two gears is very important. If they are even slightly tight probably the condenser does not turn properly and as a result of this a highly deformed signal is obtained.

It was observed that using only two stages of r.f. amplification gave a big signal-to-noise ratio and there was no appreciable change by using four stages. When properly set up the spectrometer gives a good signal.

3.2 The Phase Sensitive Detector

The circuit diagram of the phase sensitive detector and amplifier is shown in Fig. 3.

The signal from the oscillator detector, controlled at the input by an attenuator (500 K potentiometer) is first amplified by a narrow band amplifier (5693 low noise premium tube). The narrow band is obtained by the twin-Tee filter which passes all frequencies except a very small band (a few cycles around 74 c/s in the present case). The twin-T network serves as a negative feedback on the control grid of the 5693 and blocks all signal components except those in the vicinity of 74 c/s.

The amplified signal from the 5693 is then sent to a phase inverter (6SL7) in which the two control grids of the double triode are cathode coupled to each other. The two signals from the plates are at 180° from each other. Often in p.s.d. the phase invertor stage is replaced by a center tap transformer which has the same role.

The two signals at 180° from each other then go through a double cathode follower (6SL7) for impedance matching from which they proceed to the control grid of the phase detector (two 6SJ7). This stage also provides for d.c. amplification. A reference signal, which is for convenience amplified by a two stage amplifier (using a 6SN7) is fed to

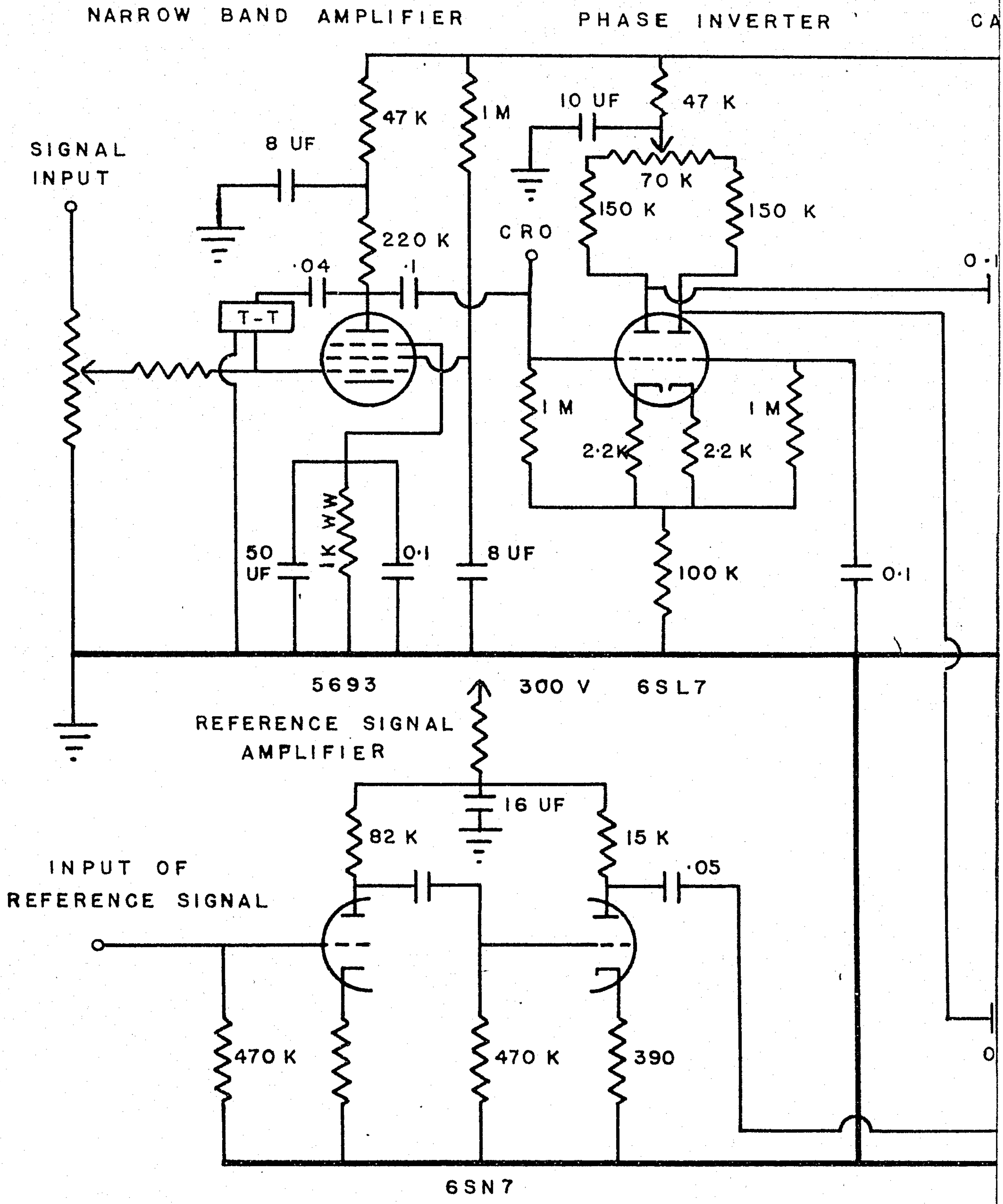
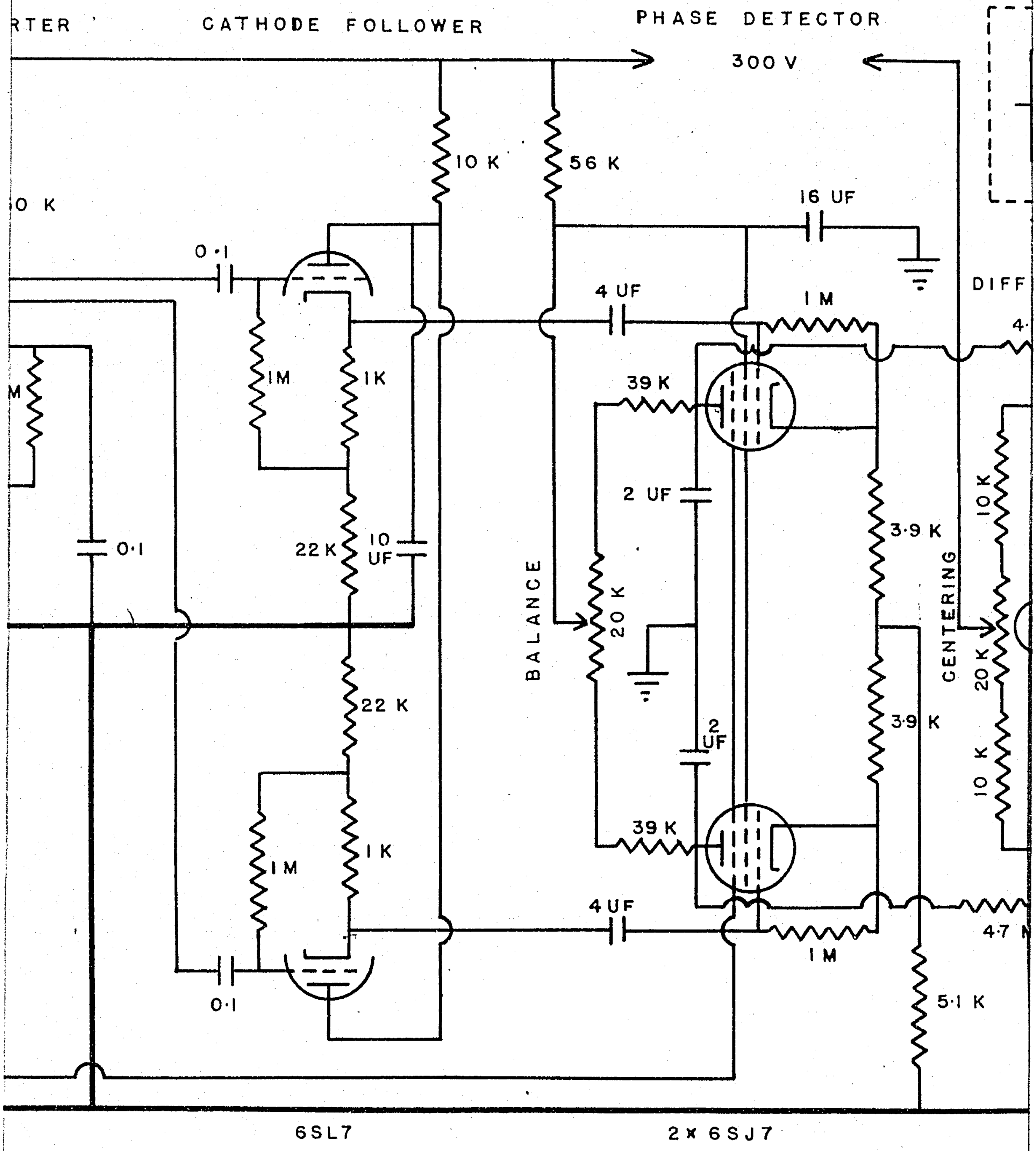
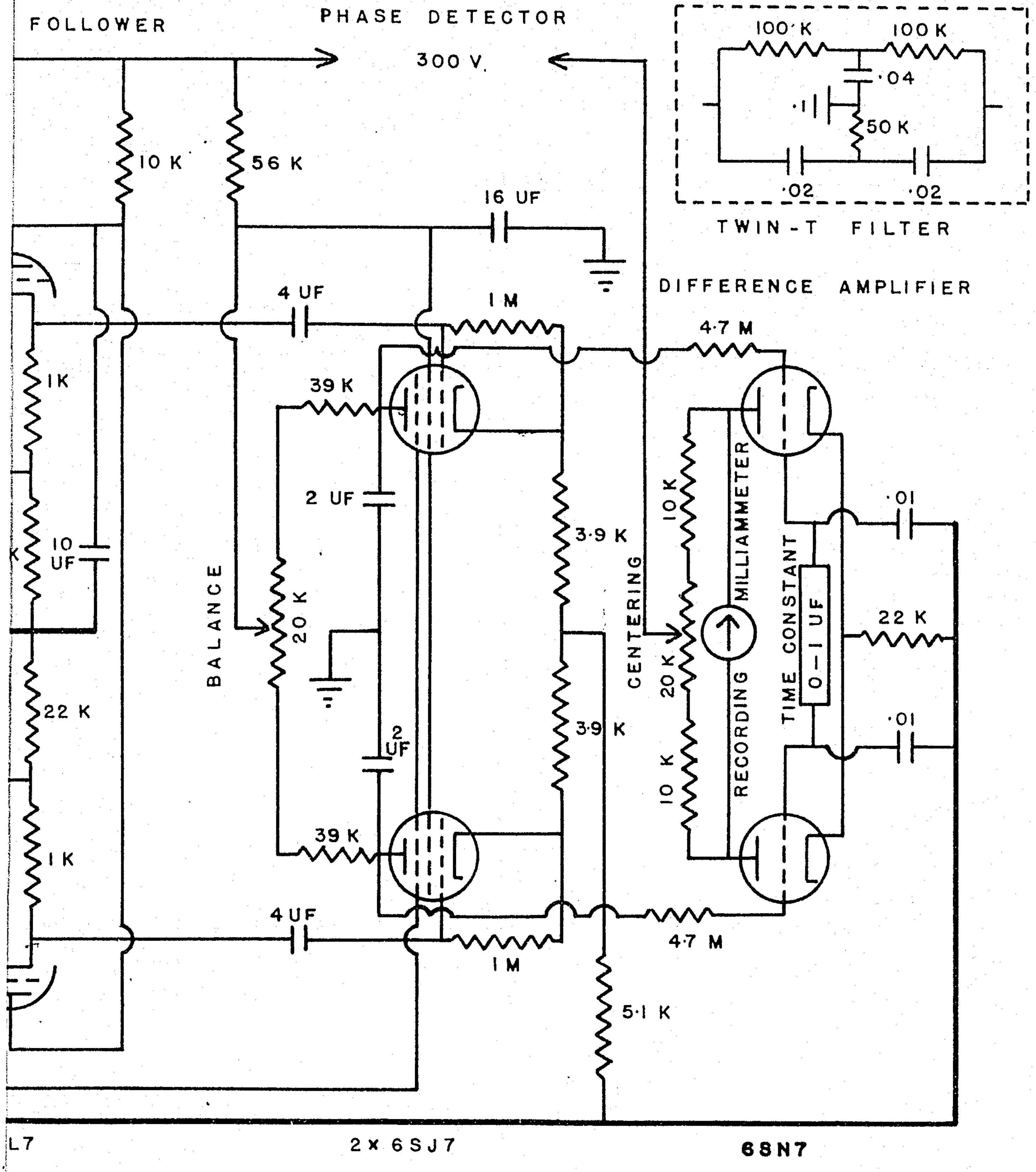


FIG. 3 - CIRCUIT DIAGRAM OF THE PHASE SENSITIV



ASE SENSITIVE AMPLIFIER ·


FOLLOWER
PHASE DETECTOR
300 V.
100 K
100 K
·04
·1
50 K
·02
·02
TWIN-T FILTER
10 K
56 K
16 UF
DIFFERENCE AMPLIFIER
4 UF
1 M
4·7 M
1 K
39 K
2 UF
10 UF
K
3·9 K
10 K
MILLIAMMETER
·01
BALANCE
20 K
CENTERING
20 K
TIME CONSTANT
0–1 UF
22 K
RECORDING
22 K
2 UF
3·9 K
10 K
·01
39 K
1 K
4 UF
1 M
4·7 M
5·1 K
L7
2 × 6SJ7
6SN7

LIFIER ·

the suppressor grid of the two 6SJ7.

The change in amplitude of the audio signal from the oscillator detector is thus translated into a d.c. amplitude difference (note the 2 µF capacitor to ground on each plate to short any a.c. component). On one tube the suppressor voltage will aid the signal of the control grid while on the other tube, (where the control signal is at 180° from the first) the reverse will be true.

Finally the d.c. signals from the two plates of the two 6SJ7 will be channelled to the d.c. amplifier or difference amplifier which was a 6SL7 (double triode).

The current through each plate load (10 K) will depend on the bias of each grid. The plate potential across the two will then be recorded by the current that will flow through the recording milliammeter in one direction or the other.

A decade consenser placed across the two control grids of the last 6SL7 together with the 4.7 M resistor will control the time constant of the difference amplifier from a few tenth of a second to a few seconds. The input signal to this circuit can be displayed on the C.R.O. after narrow band amplification.

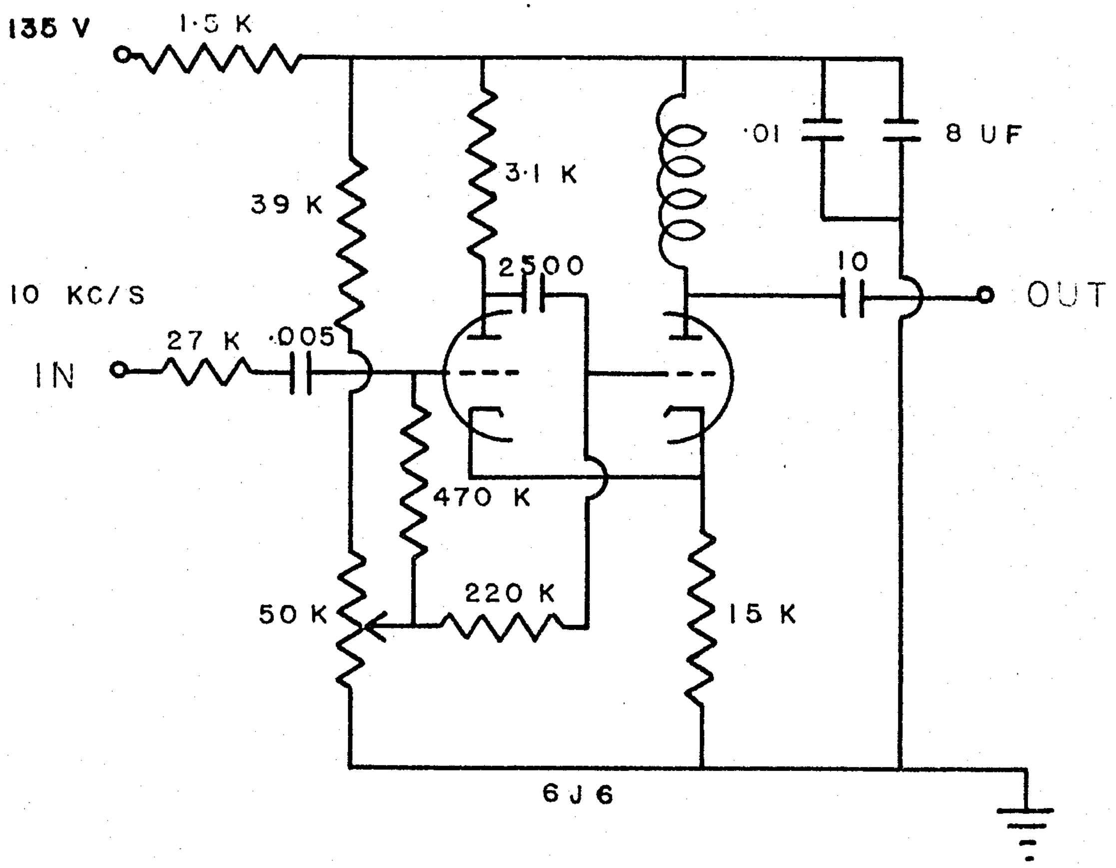
Care must be taken that the reference signal placed on the suppressor grid of the phase detector (two

6SJ7) be large (about 35 volts peak-to-peak) and yet undistorted. For that reason an output from the plate of the last stage of the 6SN7 is available for observation of this voltage on the C.R.O.

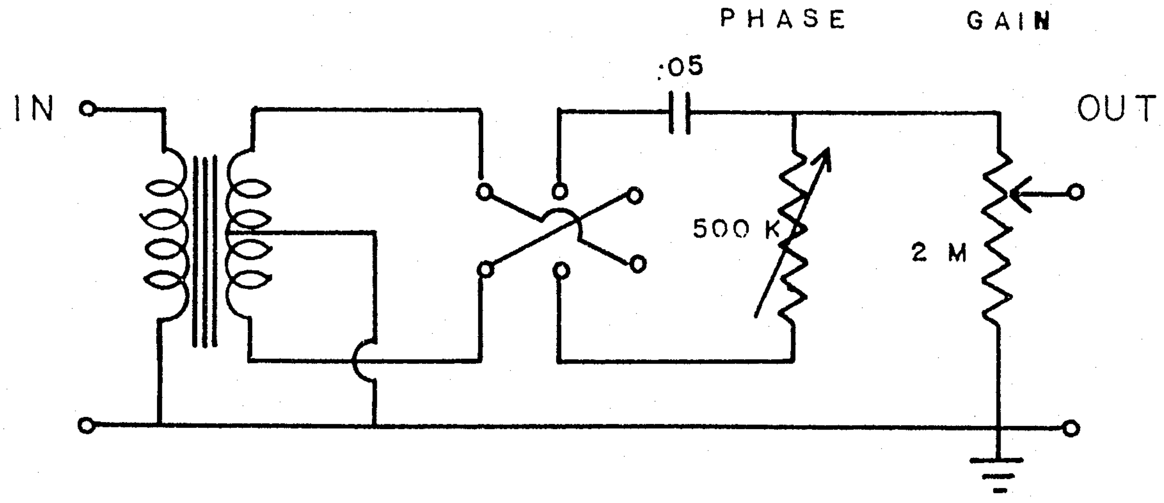
3.3 The Phase and Gain Control

From a single source of audio frequency it is necessary to obtain many sources at a given frequency to feed various parts of the spectrometer as we have seen in the discussion of the Block Diagram. These are to the power amplifier for modulation of the magnetic field, the calibrator of the oscillator detector, the reference input of the P.S.D. and the time base of the C.R.O. These signals must be at exactly the same frequency but each one must have its own amplitude and phase with respect to the others. For that we looked for a simple network that will allow us to change the phase of the input signal and a simple attenuator to control the gain. The circuit diagram has been shown in Fig. 4.

As many of these circuits may be put in parallel as is necessary, taking care that the impedance of the input transformers match that of the output of the low frequency oscillator (in the present case a Hewlett Packard No. 201 C). It is found with our arrangement that the phase and amplitude of each can be varied over a wide range without disturbing appreciably the phase and amplitude of the others.



FIG· 5 – CIRCUIT DIAGRAM OF THE FREQUENCY MULTIPLIER·



FIG· 4 – CIRCUIT DIAGRAM OF A TYPICAL PHASE AND GAIN CONTROL·

3.4 The Modulation of the Magnetic Field

The modulation of the field is accomplished by sending the 74 c/s frequency through a power amplifier to a pair of coils mounted on the pole faces of the magnet.

To find the amplitude of modulation in gauss the frequency is adjusted first on left and then on right of trace. From these frequency measurements and the known g factor of Al27, an evaluation of modulation amplitude in gauss is made. It was observed that the modulation is 3 gauss peak to peak for r.m.s. current of 36 milliamperes flowing through the coils, which in the present set up is the maximum current we can pass undistorted.

3.5 The Recording System

The first derivative of the resonance signal is recorded on the chart of the Esterline Angus recorder (One milliammeter f.s.d.). The recorder has five standard chart feeds in inches per hour or minute.

This recorder has also a pen actuated by a small electromagnet to put frequency markers on the chart.

3.6 The Power Supplies

We have used regulated power supplies (Model 29 and 28, Lamda Electronics Corp.) for the oscillator-detector and the P.S.D. circuits respectively. The behaviour of these power supplies was found satisfactory and their stability was found to be good enough not to require any line regulators.

The filaments of all the tubes are heated by 6 volts D.C. batteries to avoid the 60 cycle A.C. ripple. For long periods of operation of the spectrometer, the batteries are continuously charged by the battery eliminators. This method of simultaneously charging the batteries as the filaments of the tubes are being heated is quite essential because we observed that the oscillator performance is very sensitive to the filament voltage.

4. The Preparation of Samples

While working with the spectrometer we looked for signals either from salts of the metal or the metal itself. The salt is dissolved in distilled water and a concentrated solution is used to look for the signal.

For the study of line shape and resonance frequency in metals it becomes necessary that the powder used has very fine particle size. If size of the particles is greater than the skin depth at the given frequency and temperature, only the nuclei which lie at the top of the surface will absorb energy and the intensity of the signal would be decreased. The skin depth is calculated as follows;

$$d = 5033\sqrt{\frac{\rho}{\mu f}}$$

where d is the skin depth in cms, ρ is the resistivity in ohm cm. and f is the frequency in cycles. μ is permeability and its value is approximately unity for non-magnetic materials. For a typical case of Al27, the skin depth at 7.5 Mc/s (approximate n.m.r. frequency of Al27 in our magnet) and 20° C is found to be $\sim 3 \times 10^{-3}$ cms.

The bigger size of the particles can also affect the shape of the absorption line. Bloembergen (1952) has shown that if the dimensions of the particles are not small compared with the skin depth, the absorption line may become distorted and shifted.

A simple motor driven filing machine was built to obtain fine powdered samples. A few trial runs were made to file some commercial Aluminium available in the department. The filings were then passed through a Tyler Standard Screen, No. 325 of hole size .043 mm. Nearly all the filings passed through the screen indicating an average particle size smaller than the screen size.

To make sure that there was no iron present in the filed powder, the following test was performed;

The powder was treated with dilute sulphuric acid and then neutralized with ammonium hydroxide. Adding a drop of ammonium thiocyanate did not result in red colour, thus confirming the absence of iron particles from the file.

5. The Measurement of Frequency

The measurements of frequency with the spectrometer described in this thesis where a permanent magnet is used requires that frequency markers be put on the chart, where the signal is recorded, at sufficiently small interval to allow for good interpolation. By far the best method in such a case is one in which the r.f. from the oscillator detector is mixed in a receiver with a signal of known frequency and the beat frequency is measured.

For Al27 for instance the resonance frequency in our magnet is of the order of 7.5 Mc/s. The Knight shift for pure Al27 is 0.162% (Knight 1956) which means that the line in the metal is about 12 kc/s higher than the salt. The changes from this shift for dilute alloys are probably quite small may be of the order of 100 c/s. The accuracy we must aim for is thus about 10 c/s in 7.5 Mc/s or approximately 1 part per million. A better accuracy is not necessary as the center of the line cannot be determined to better than a few tenths of cycles/s since the metal line is wide.

This accuracy is better than what can be obtained with army type of frequency meter and it can be obtained easily with a simple arrangement as shown in Fig. 1 and explained in Section 3 of this Chapter. We will give below a short discussion of the various components and of the method of operation.

5.1 The Components of the Frequency Meter

The basic component is an oscillator capable of giving a fundamental frequency with great stability. This is available commercially. The Hewlett Packard Low Frequency Standard has an oscillator which is controlled by a crystal held at constant temperature in an oven. It gives out signals of 10 c/s, 100 c/s, 1 kc/s, 10 kc/s and 100 kc/s with a claimed stability of 1 part per million over a period of a week. Using a frequency comparator it can be cheched against W.W.V. for absolute value.

A 10 kc/s from this standard has then to be multiplied to give high harmonics in the region of 7.5 Mc/s. These harmonics can now be mixed in a communication receiver with the r.f. signal of the oscillator-detector. The output from the receiver is then sent to a C.R.O. the time base of which is driven by a 1 kc/s or 100 c/s from the standard. Lissajous patterns can be counted and frequency markers put on the recorder's chart at 100 or 1000 c/s intervals.

To obtain high harmonics of a given frequency the sine wave from the standard is passed through a square wave generator having a rise time inversely proportional to the frequency of the high harmonics desired. This square wave when analysed by Fourier analysis is found to be rich in harmonics of 10 kc/s in the desired range.

To obtain this fast rise time ($\sim 0.1\ \mu$ s) we used the following harmonic generator circuit which is shown in Fig. 5. The sinusoidal signal is applied on the grid of the 6J6 which operates as a class C amplifier. It is amplified again in the second stage the plate load of which is a small radio frequency coil which produces a ringing around 10 Mc/s and improves the harmonic content in the high frequencies.

The signal from this amplifier is loosely coupled to the receiver. The requirements for the receiver are good sensitivity and stability and a band width around 10 kc/s. The Eddystone No. 840 A satisfies all these requirements. It has the advantage of good reproducible tuning with a sufficiently good vernier.

5.2 The Method of Operation

The first step is to identify the various harmonics of 10 kc/s on the receiver. This is easily done using the receiver in the C.W. operation and calibrating with B.C. 221 which gives a reliable measurement of each kc/s ± 100 cycles.

Once the vernier of the receiver is thus calibrated, it remains only to set the receiver at the proper position and interpret the Lissajous patterns on the C.R.O. to register every 100 c/s or 1 kc/s on the chart with markers. The receiver need be reset only after the frequency has changed by 10 kc/s.

An illustration of this technique can be seen on Plate I where a signal of A127 is recorded from a solution of $AlCl_3$. It can be seen that by careful interpolation the frequency of the center of the line (which is the first derivative of the absorption curve) is found within 10 c/s. Also the line width can be determined with accuracy if we define it as the distance between maximum and minimum of the derivative.

6. The Magnet

The permanent magnet used in this work is on loan from Atomic Energy Commision. It has been manufactured by Indiana Steel Product (Indiana) and it was designed to have the best homogeneity over the largest possible volume.

The gap of the magnet is 2" and the pole faces are 8 inches in diameter while the pole pieces are 12" in diameter. The yoke which serves as a return path for the magnetic lines of flux is rectangular and of rectangular cross-section of 14" by 4".

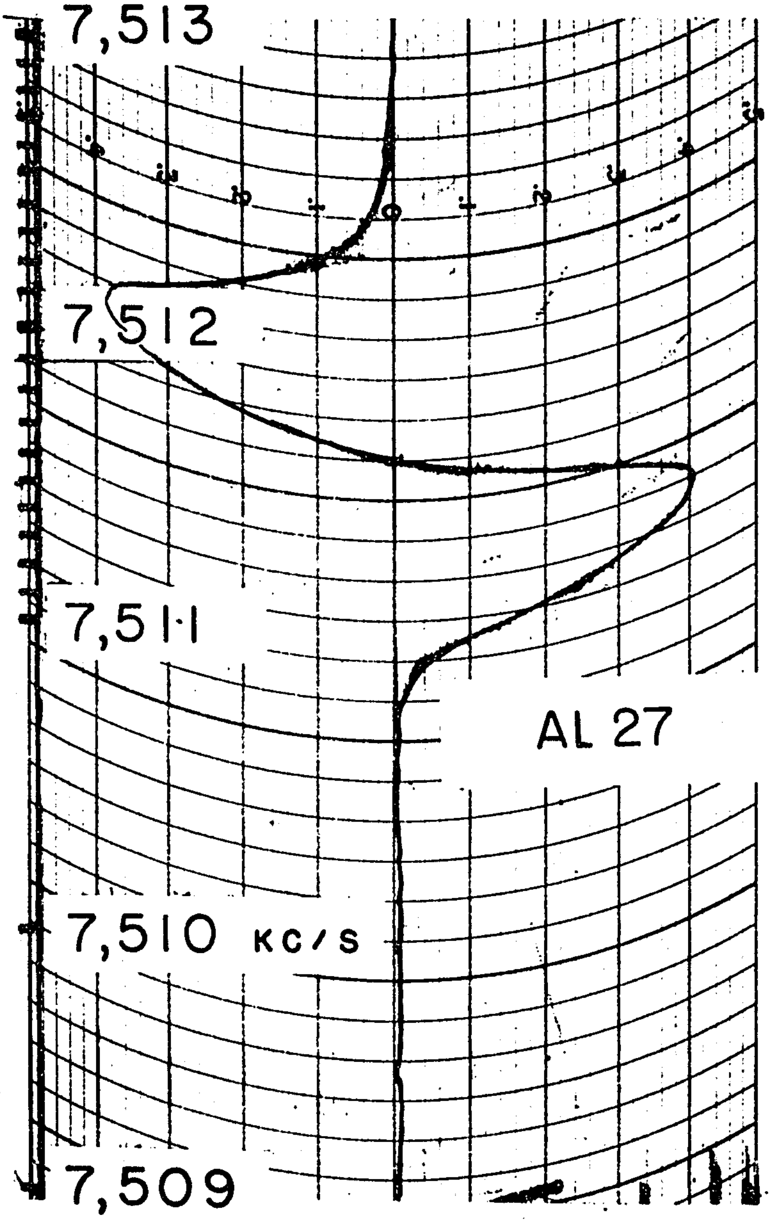


Plate I

Chart Showing Frequency Measurements Technique

Al27 Signal with frequency markers every kc/s from 7,509 to 7,513 and with frequency markers every 100 c/s from 7,511 to 7,513. The center frequency is found to be 7511.90 kc/s ± 10 c/s.

For convenience the magnet has been mounted horizontally on a wooden bed.

We thought it would be advisalbe to investigate as much as possible the state of the magnetic field before starting our investigations because of the unknown past history of the magnet since it left the manufacturer. Our requirements as far as homogeneity is concerned are mild as in our investigation of the width of the n.m.r. lines we search are seldom less than one gauss. For making a detailed examination of the resonance line, it is essential that the magnetic field homogeneity throughout the volume which the specimen occupies be better than the width of the line.

The nature of the measurements involved in Knight shift measurements requires that the field be as stable as possible during the measurements. Gutowsky, Meyer and McClure (1953) say that the variation of the magnetic field of a permanent magnet with temperature is approximately one part in five thousand per degree centigrade. Our laboratory being subjected to change of temperature of about five degree centigrade at least for 24 hours period during the winter and some time as much as 25° C during the summer, the rate of change of the field with temperature may be up to 2 gauss/h. This is certainly not acceptable, as in measuring the shifts the method is to scan continuously in frequency and recording first the signal in a solution and then in the metal, over a period of approximately 15 minutes or more. Because of the accuracy with which we measure these shifts in various alloys, a temperature variation of 10 milligauss per hour is tolerable.

It was thus decided to study both the temperature variation of the magnet and its homogeneity. The result of this investigation is detailed in Chapter III.

CHAPTER III

A Study of the Performance of the Spectrometer

1. Introduction

We have already stated in Chapter II what are the requirements of the spectrometer for the proposed investigation. We have also shown that the measurement of frequency was possible with the present set up to the degree of accuracy required.

In this chapter we will discuss the behaviour of the other components of the spectrometer. First we will discuss the detection of signals for various nuclei, in Section 2. Then a very important part of the spectrometer, the magnetic field of our permanent magnet is studied in Section 3. Finally a typical measurement of the Knight shift on Aluminium was accomplished and the results obtained are discussed in Section 4.

We will thus show that the spectrometer, even if it is not ideal, can be put to do some useful investigation of the effects of magnetic impurities on the n.m.r. line of metals.

2. The Detection of Various Signals

The detection of n.m.r. signals is difficult because in general this signal is of the order of magnitude of the noise level of the oscillator detector. Thus unless some conditions are achieved the signal is indistinguishable from the noise. The considerations that improve the signal to noise ratio have been discussed at length by BPP (1948) and by Andrews (1956). It requires that the filling factor of the sample coil be as large as possible to get the maximum number of nuclei to absorb the r.f. energy. The Q or quality factor of the coil must be high and the art of making good coils has been discussed by many authors. The level of oscillation must also meet some requirements based on T_1 and T_2 to avoid saturation. The fact that the Pound-Knight arrangement does not permit very low levels of oscillation restrict the number of nuclei from which we can get a good signal and this explains in part our unsuccessful search for a signal from Mg25.

The amplitude of modulation has also to be taken into consideration to get a strong signal, specially in the case of narrow band detection.

The amplitude of modulation, the requirements on the coil, the amplitude of the r.f. oscillation, the amplification of the r.f. signal, the amplitude of the a.f. signal in the phase sensitive detector and the time constant are all variables that have to be optimized to get the best signal-to-noise as well as the most faithful line shape.

The setting of these variables can be in part obtained from theoretical considerations but in practice there is a good deal of trial and error.

By far the easiest signal to detect is that of protons. Two traces from protons are shown on Plate II. Here the resonance frequency in our magnet is approximately 28.8 Mc/s. It is difficult to evaluate the signal-to-noise in such a case but it is certainly excellent. This was observed from distilled water to which a small amount of paramagnetic impurity has been added, since the paramagnetic ions in water shorten time T_1. This widens the line, increases the signal-to-noise ratio and increases the saturation level.

The signal of Al27 is shown also on Plate II. Our objective was to get a good signal from this nuclei and again the signal-to-noise is difficult to evaluate and certainly is sufficient for our purpose. Two similar signals appear on the chart shown.

Finally on Plate II we can see the signal obtained from Na23. The resonance frequency here is around 7.6 Mc/s. The signal-to-noise ratio is only approximately 15:1. This poorer ratio is expected. The relative sensitivity for an equal number of nuclei of Na23 as compared to proton is known to be 0.09 in the same field (cf for instance the NMR Table, 3rd edition, published by Varian Associates, Palo Alto, California)

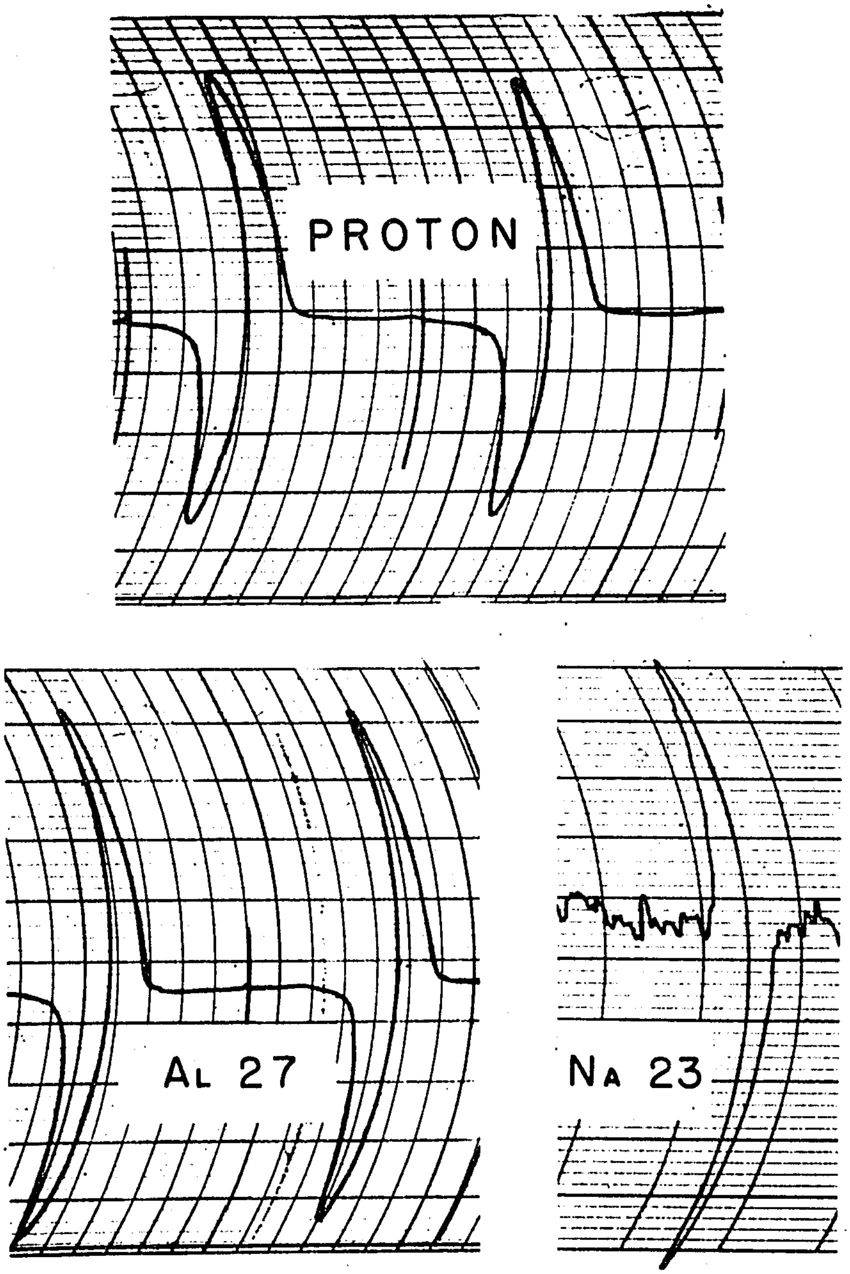


Plate II

Chart Recordings of Signals from H1, Al27 and Na23

Typical signals from H1 in distilled water, Al27 in a $AlCl_3$ solution and Na23 in a NaCl solution. Notice better signal-to-noise of protons and Aluminium as compared to sodium.

Even then the spectrometer could be used for the study of sodium. It must be remarked that better ratio could be achieved with this spectrometer for Na23 by obtaining better conditions of operations for which we did not look in this particular case.

We have focussed our attention on Al27. The next step was to look for the signal from a metallic sample of aluminium. As we have already explained in Section 4 of Chapter II, to get a good signal from a metal the sample must be in the form of small particles isolated from each other. With aluminium this is easily achieved as a coating of aluminium oxide will create sufficient insulation for the particles. The easiest way to obtain small particles of aluminium is to file a piece of the metal with a fine grain file. The particles obtained are of the desired size and when looked at under a microscope they appear as the turnings that come out of a lathe.

On Plate III we have examples of the signal from metallic aluminium. In this upper trace we have a signal from aluminium dust which was available commercially. This dust when looked at under the microscope looked like small aggregates of various smooth forms. The particle size was comparable to the filing we have obtained. Below on the left of this plate we see the signal from our filings

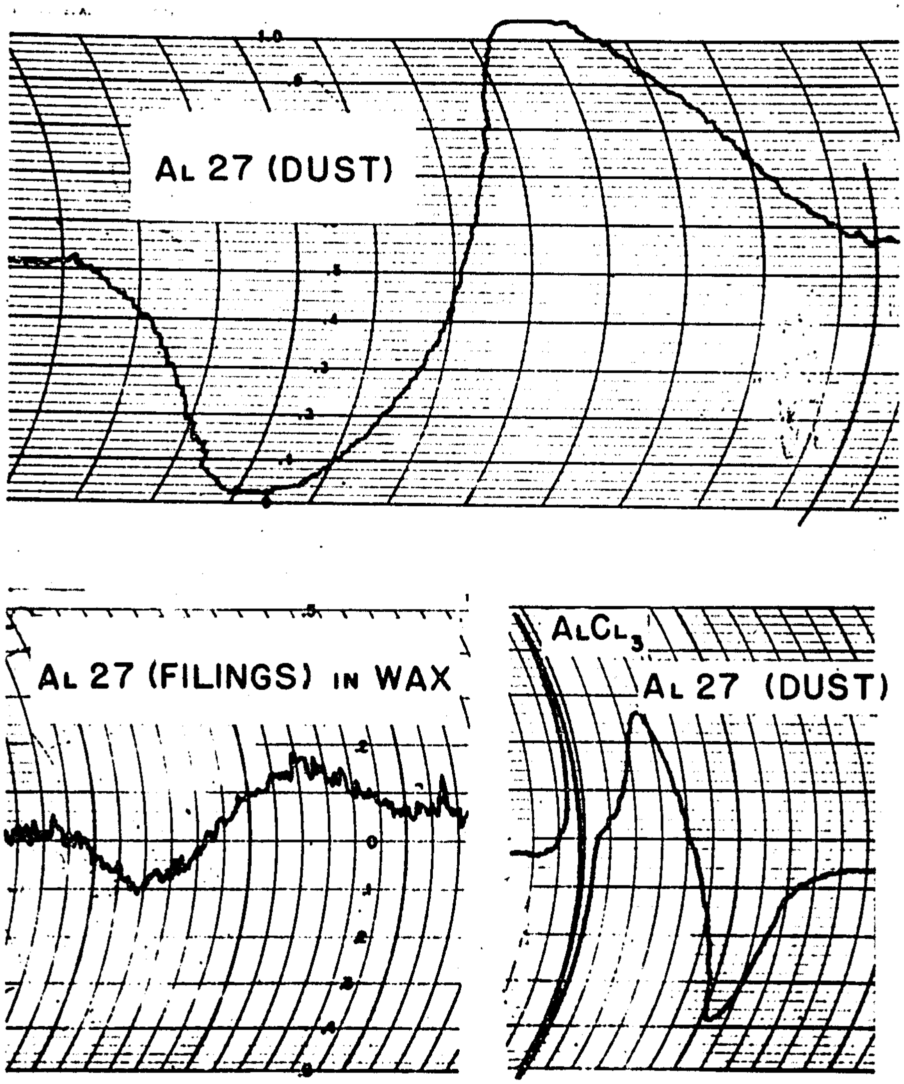


Plate III

Al27 Signal in Metals

Al27 Signals from commercial dry dust and from aluminium filed in the laboratory and cast in wax. Also a comparison between Al27 in AlCl$_3$ solution and aluminium commercial dust in which the Knight shift is exhibited.

which was poured into solid paraffin for convenience of handling. The latter gives a poorer signal as compared to the commercial dust.

We believe that the difference comes essentially from the fact that our filings having been cold worked are in a strained state and that the quadrupolar effect is responsible for the poorer signal. Annealing the sample will undoubtedly improve the signal.

Finally on this Plate on the lower right is displayed the signal from Al27 in $AlCl_3$ and in aluminium dust as the frequency is increased continuously. The Knight shift is exhibited here very clearly and it is from such trace that the shift computed in Section 4 was measured.

3. The Magnetic Field of the Permanent Magnet

The requirements for the magnetic field for the proposed investigation are as we have mentionned before that the field should be reasonably stable over a period of time and homogeneous over the volume of the sample. We will discuss these two problems in turns.

3.1. Temperature Variation of the Magnetic Field

A series of early experiments revealed a magnetic field fluctuation over short period of time which precluded the possibility of carrying out the measurements.

A plywood box was built around the magnet and filled with "vermiculite", a commercial heat insulator. This brought some improvement to the performance but it was still inadequate during the summer months. The box containing the magnet was later surrounded by an "oven". i.e. a chamber, made of plywood sheet and insulated with two inches of glasswool. A minimum air gap of 4" was left between this wall and the magnet box. An access to the magnet gap was left, large enough to allow for replacement of the sample container and for the tables on which the oscillator detector is located.

A heater and a fan were placed inside the oven together with a thermistor element for a thermostat. The oven is to be maintained at a constant temperature (above the ambient temperature) within a tenth of a degree centigrade or better. The thermistor was placed in an arm of a d.c. bridge which actuated a relay to switch on and off a heater (light bulb). The d.c. amplifier in the bridge proved unstable for operation over a long period and will be replaced by a commercial a.c. bridge with a better temperature sensing element. During the winter months however, it is found that a temperature control of the oven is not necessary.

The temperature variation of the magnetic field can only be defined as the variation with the average temperature of the magnet. The latter temperature is not easily available. Instead we have always considered the variation with the temperature of one end of the magnet where a 1" diameter hole through the yoke was made to a depth of 4" allowing a thermistor to be placed in that space. This thermistor thermometer element was read with a Wheatstone bridge. All our knowledge of the temperature variation is based on this temperature reading which is not necessarily the average temperature of the magnet but only served as an indication of it. What complicates the problem of finding a better parameter is the fact that the gap of the magnet is of necessity exposed to the ambient temperature. This creates in the whole magnet an unknown and varying temperature gradient.

The study of the performance of the magnet as far as temperature variation of the field is concerned could be carried out and an improvement of the measurement of the temperature was not necessary.

Performance with Regard to Temperature

With the insulation described above, the temperature variation of the magnetic field over long periods of time (5 - 10 hours) was found to be well within the limits imposed by the measurements described in this thesis without any control of the oven temperature during the winter months.

We studied the variation of the magnetic field as a function of time, as observed by taking the resonance frequency of Al27 in $AlCl_3$ solution at a given point in the field. In a typical case the field was found to very by less than 20 milligauss/hour.

The temperature variation of the magnetic field with the temperature measured by a thermistor inside the magnet was also studied. A field variation temperature coefficient of 1.57 Gauss/° C was obtained in this case within the limitation explained above.

On the following Table is given the temperature variation of the magnet in milligauss, with time and with room temperature as a typical example. Variation of this order are acceptable as we have mentioned above.

Table

Time	Room Temp. °C	Milligauss
2.50 P.M.	29.20	0
3.30 P.M.	28.40	-36
3.45 P.M.	28.20	-36
4.20 P.M.	28.20	-54
4.30 P.M.	28.20	-45
6.35 P.M.	28.05	-54
6.45 P.M.	28.25	-54
6.53 P.M.	28.25	-54
6.58 P.M.	28.30	-63

3.2. The Homogeneity of the Field

According to Knight (1956) the field over the volume of the sample (say about 2 cc.) should not very by more than 0.1 gauss. It is very important to explore the field of our magnet to find out if this requirement is fulfilled and if so to find out a suitable region to place our sample for investigation.

N.M.R. affords one of the best methods of measuring the value of the magnetic field if the gyromagnetic ratio g of a given nuclear isotope is known with accuracy since the resonance frequency ν can be measured accurately and H, the magnetic field is obtained readily since $H_o = \frac{h\nu_o}{g\beta}$ where β is the nuclear magneton.

To investigate the homogeneity of the field of a magnet the principle is the following;

A sample is located in the field and the frequency of resonance is measured. By successively placing the sample at different locations, a map of the magnitude of the field can be obtained. Two methods were tried to perform this mapping.

In the first method the field is modulated at large amplitude and the signal is displayed on an oscilloscope. The position of the center of the resonance line on the horizontal co-ordinate of the C.R.O. is then function of the frequency. A calibration of this co-ordinate as function of frequency is in principle easily accomplished by choosing the frequency of the r.f. oscillator so as to get the signal to coincide with the beginning and with the end of the trace, measuring in each case the frequency of the r.f. oscillator. Since the audio frequency signal is common to the modulation of the field and to the horizontal drive of the C.R.O., the horizontal co-ordinate on the screen is proportional to the frequency and hence will be proportional to the field if now the specimen is moved in the field gap keeping the oscillator at a fixed frequency. The position of the center of resonance with respect to the horizontal trace is noted for various positions of the sample in the gap and the magnetic field can be deduced.

This method is rapid and sufficiently accurate in so far as the frequency of the r.f. oscillator is stable during the measurement but is not capable of enough accuracy. It was abandoned.

The second method consists in using the narrow band amplifier, a small field modulation and displaying the signal on the chart recorder for various locations of the sample in the gap. An accurate frequency measurement (see Section 5.2 of Chapter II.) can then be performed on each trace. With the result of many observations, a map of the field can be done.

This method has the advantage of being more accurate than the first one and will not suffer from possible drifts of the r.f. oscillator. Its disadvantage is the time involved, since each display of the line involves 10 to 15 minutes.

Both methods were tried. The C.R.O. method was tried with a proton signal and the field was investigated over a large region of the total gap. The results of this investigation were however found inconsistent probably due to frequency drifts. In an effort to understand these results it was decided to use the second method which indeed gave us the information required.

The Reference Axes in the Magnet Gap

To investigate the field and locate the position in the gap with great accuracy, a set of three support plates for the r.f. oscillator box was designed, each capable of a movement along one axis.

The lower support plate moves up and down on a system of screws and sprockets linked together by a brass bicycle chain drive for a steady motion. The next support plate slides over the lower one along a horizontal direction and the last support plate moves at right angle to the second one in a direction perpendicular to the other two. On each plate a pointer is fixed and moves with the plate on a fine ruler.

In this way the location of the sample in the gap can be read and reproduced to better than 0.05 cm in all three directions.

We have labelled the axes in the gap as follows for convenience:

X-axis	is parallel to the axis of the pole pieces of the magnet
Y-axis	is at right angle to the x-axis in the horizontal plane
Z-axis	is at right angle to the x-y plane and hence is vertical.

No effort was made to find the geometrical center of the magnet gap which is not easily accessible anyway. Instead we have set arbitrarily the origin of our axes on our reference scale, this origin being reasonably close to what we estimate to be the geometrical center of the magnet. All our measurements are with reference to this arbitrary origin which read $x = 2.50$ cm, $y = 0.00$ cm and $z = 9.60$ cm. on the rulers. On Fig. 6 and Fig. 7 the distance is always with reference to this origin $X = 0$, $Y = 0$, $Z = 0$.

The Magnetic Field Map

As a first exploration of the field, the sample a cylinder 1 cm. long with 4 mm. diameter of saturated

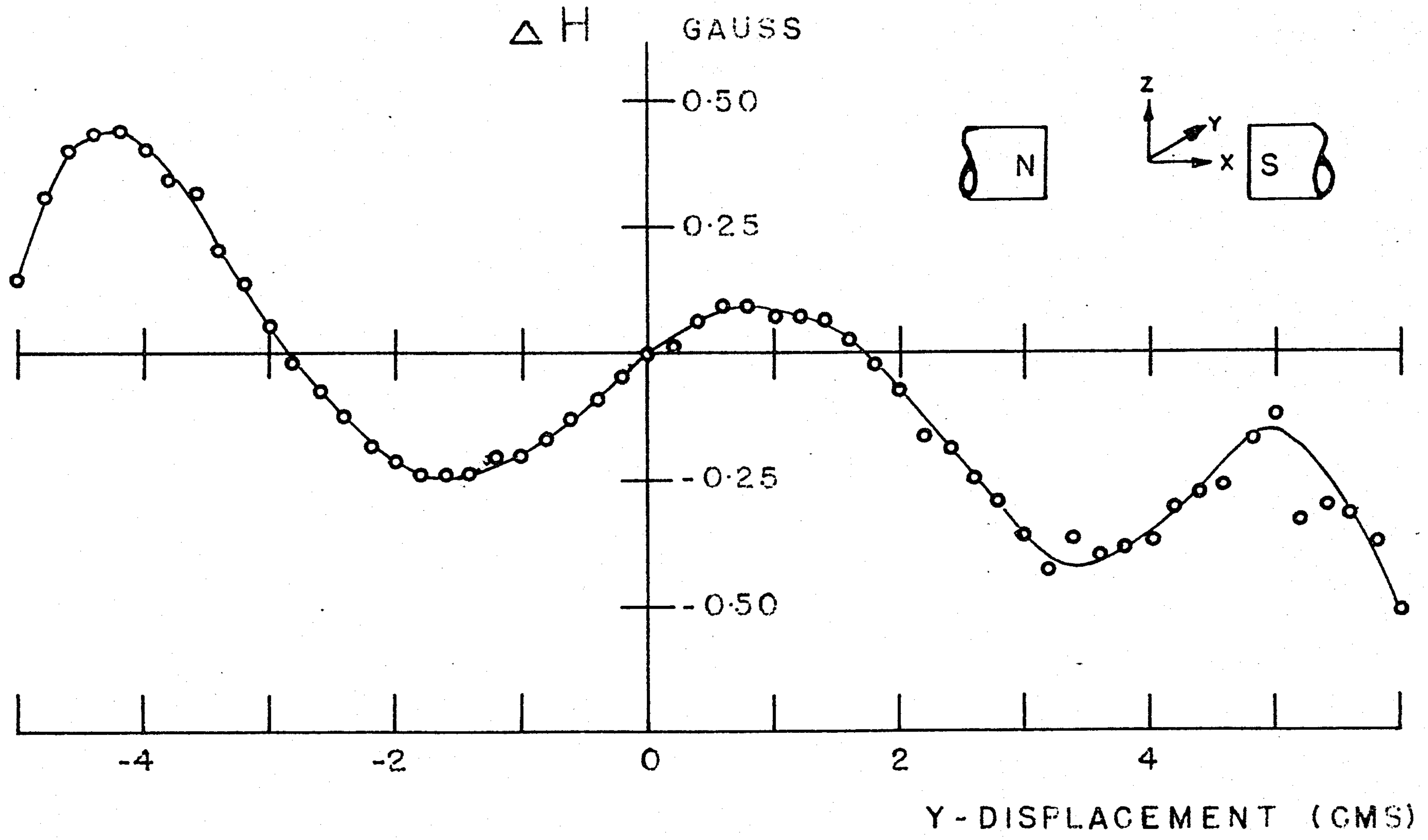


FIGURE 6 – FIELD VARIATION ALONG Y-AXIS FOR X = 2·5 CMS AND Z = 9·6 CMS.

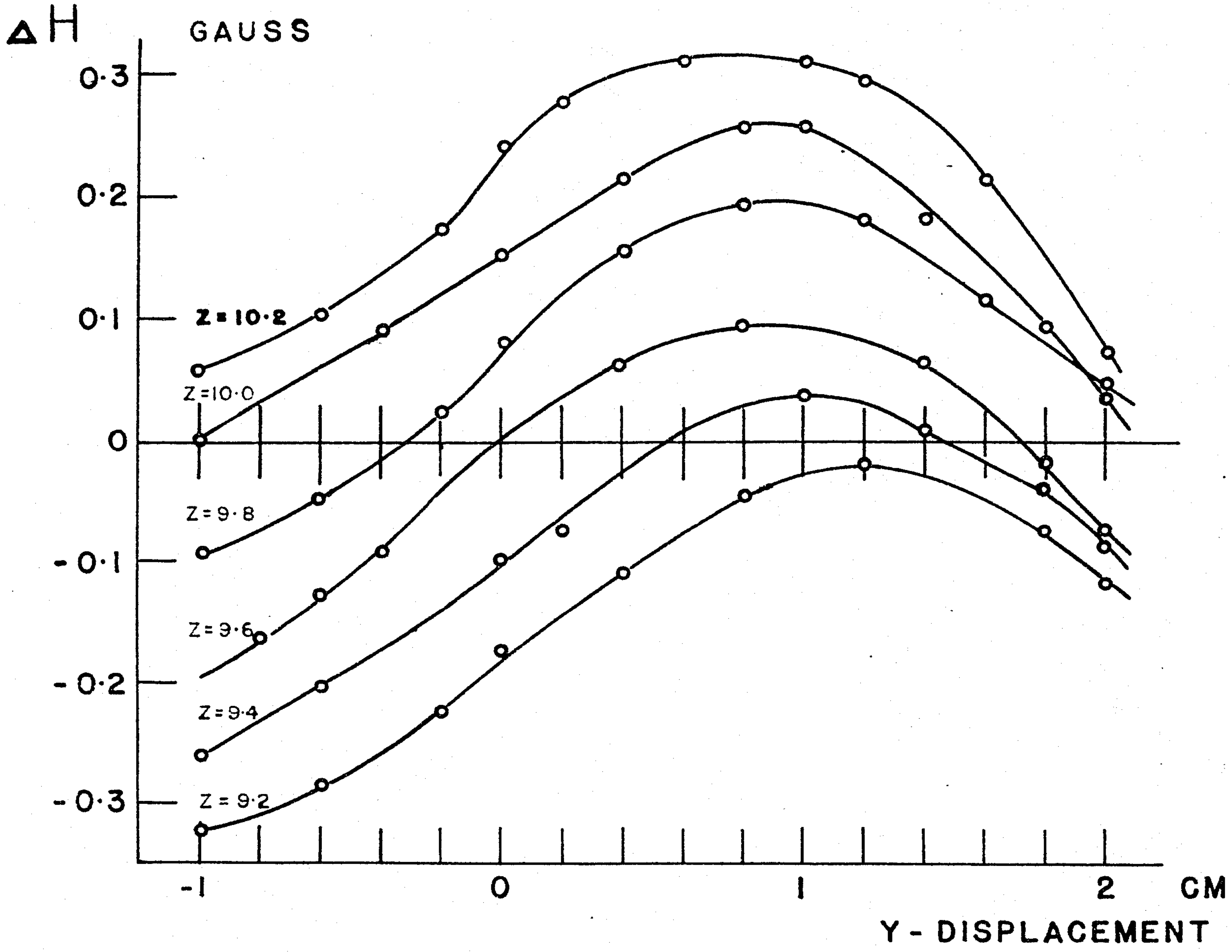


FIGURE 7 – FIELD VARIATION ALONG Y-AXIS FOR DIFFERENT Z-VALUES.

solution of $AlCl_3$ in water was placed at the origin and the A127 signal obtained on the chart and its frequency was determined with maximum accuracy available (± 10 c/s).

From this point the sample was moved by 2 mm steps in the horizontal direction along the Y-axis as long as the inhomogeneity of the field was not so large so as to deform the signal excessively and the frequency was measured with the maximum accuracy at each step. It was also moved on the other side of the origin as far as practicable. For each point, the room temperature and the magnet temperature were recorded. At regular intervals of time, the frequency at the origin was measured to allow for temperature correction when plotting the results.

The result of this preliminary exploration of the field is shown on Fig. 6 which is a plot of the deviation of the field H at point (0, Y, 0) from the value H_0 of the field at the origin in milligauss against Y. It is seen from this graph that the field is constant to better than 1 gauss in 6770 gauss for a radius of approximately 7 cm (the pole face has a diameter of 20 cm) around the center. Also this graph gives a detailed picture of the field along that line.

To have a better knowledge of the region where to place our sample, we decided to investigate in greater detail the region between Y = -1 cm to 2 cm, from Z = 9.2 to Z = 10.2 cm. The result of this investigation is given on Fig. 7 where again the difference H (0,Y,Z) -H (0,0,0) is given in gauss as a function of Y for various values of Z after allowing for temperature corrections. We see from this graph that if the sample is located anywhere in the region mapped on this graph, the field in the whole volume of the sample should not vary by more than about 0.5 gauss which is probably acceptable.

The homogeneity of the field is not of course too satisfactory if we take as necessary the requirements given by Knight. However, since the metal n.m.r. line is in general of the order 10 gauss wide it may not give us a reliable measurement of the absolute width, but it will not make impossible the study of the effect of magnetic impurities on the width of the line which is our final purpose.

From that point of view this survey of the field indicates that the magnetic field of the magnet is sufficiently homogeneous for our proposed investigation, at least in the region surveyed.

4. A Trial Run on the Measurement of the Knight Shift in Aluminium

As mentioned earlier, the aim of this thesis was to assemble a spectrometer capable of measuring the metallic shift and the line width in some dilute binary alloys (Al-Mn) and thus to study the effect of magnetic impurities in metals. We made a trial run to see if the present spectrometer is good enough for these measurements in Aluminium.

For an accurate measurement of Knight shift in metals it is very important that both the metal and its salt be placed in the gap of the magnet at the same position so that it could be assumed that the external field is the same for both of them and the shift arises essentially from the extra field in the metal due to the interaction of the conduction electrons at the Fermi Level with the nuclei. This was done by placing some commercial Aluminium dust and some $AlCl_3$ solution in the same sample tube. The dust was tightly packed in the tube to have a good filling factor and four small capillary tubes containing a concentrated solution of $AlCl_3$ were placed inside the dust. The sample tube was cylindrical and 1 cm high and 0.4 cm in diameter. The position of the sample coil in the gap was $Z = 9.6$, $Y = 0$ and $X = 2.5$ cm. It will be recalled that this is what we call our zero position in the gap and all the measurements for the study of the homogeneity of the field were made with reference to this point.

Various trials were made with different amplitudes of modulation, r.f. levels and time constants until a good signals from both the salt and metal were obtained. Frequency markers were put on the chart as described in Section 5 of Chapter II.

The result of a good run was then analysed. Because of the small size of the samples a signal-to-noise of only about 10:1 could be achieved. This makes the determination of the center of the signals somewhat uncertain. In spite of that the agreement with the known value for the shift in pure aluminium which is 0.162% (Teeters 1955) is good. We found 0.164 ± 0.001% for the shift.

It should be remarked that our sample is of unknown purity and this may have some small influence on the shift. The agreement is thus quite reasonable and indicates that the apparatus is well adapted for the proposed investigation.

The measurement of the line width of the signal in the metal, defined as the distance between the maximum and the minimum of the trace, was difficult to evaluate in this particular case. A value of 9.1 ± 0.5 gauss was obtained. It is difficult to do an exact comparison with published values since the line width may depend on the impurity content and also because the homogeneity of the magnetic field over the sample may cause a spurious extra broadening. However the value obtained is reasonable and there should be no major difficulties in studying the variation of the width against concentration of impurities and against the temperature in this spectrometer as it is proposed.

CONCLUSIONS

In this thesis we have given a critical analysis of the behaviour and possibilities of the assembled Pound-Knight spectrometer. It has been successfully used to study the homogeneity of the magnetic field of the permanent magnet. The field of the magnet is perhaps not as homogeneous as would be necessary for exact measurements of the absolute value of the line width but is good enough to study the variation of the width in metals by addition of magnetic impurities.

The spectrometer was also used to study the temperature variation of the magnetic field. It is concluded that with the present arrangement for insulating the magnet it will be possible to use the spectrometer without any temperature control of the oven during the winter months but in summer months such a temperature control would become necessary.

With the present set up of frequency measurement it is possible to get the required accuracy of approximately 1 part per million. The line shift can be measured more accurately than the line width in case of aluminium. The spectrometer gives a good signal-to-noise ratio and its resolution is sufficient enough for the Knight shift investigations.

We thus hope that the spectrometer is in the state where it can be used for measuring the line shift and line width of Al27 line in Al-Mn and Al-Fe alloys at room temperature.

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