

(5) As in comparing the moments of neutron, proton, and deuteron, nuclear induction can well be developed as a simple and practical method to calibrate and measure high magnetic fields with great accuracy, and to apply it, for example, in the construction of cyclotrons and mass spectrographs.

There are unquestionably more problems which will become tangible in further development of the new electromagnetic effects. The fact that they are simple to obtain and require only very modest equipment should make it possible for many investigators to enter this field of research.

PHYSICAL REVIEW VOLUME 70, NUMBERS 7 AND 8 OCTOBER 1 AND 15, 1946

## The Nuclear Induction Experiment

F. BLOCH, W. W. HANSEN, AND M. PACKARD  
*Stanford University, California*

(Received July 19, 1946)

The phenomenon of nuclear induction has been studied experimentally. The apparatus used is described, both as to principle and detail. Experiments have been carried out in which the signals from protons contained in a variety of substances were observed. The results show the role played by the relaxation time, which was found to vary between about  $10^{-6}$  second and many seconds.

### INTRODUCTION

IN this paper we aim to describe certain experiments designed to study the phenomenon of nuclear induction, the theory of which is described in the preceding paper. While it will be assumed that this paper, hereafter referred to as I, is familiar to the reader, we will not hesitate to repeat those few formulae which are of immediate importance for the present paper. We start, then, by giving the reasons for the selection of the general methods used and follow this by a brief description of specific apparatus. Finally, the results are described in detail.

### METHOD

If matter be placed in a magnetic field  $H_0$ , in the  $z$  direction, the nuclear magnetic moments will tend to orient themselves parallel to the field. In matter of normal density, thermal equilibrium may be established, in which case there will be a paramagnetic polarization in the  $z$  direction

$$M_0 = \chi H_0. \quad (1)$$

If now we superimpose an oscillating magnetic field in the  $x$  direction

$$H_x = 2H_1 \cos \omega t, \quad (2)$$

we can expect the polarization vector to deviate appreciably from the  $z$  direction if the  $z$  field  $H_0$  approaches the resonance value  $H^*$  given by

$$|\gamma| H^* = \omega, \quad (3)$$

where  $\gamma$ , the gyromagnetic ratio, is the ratio of nuclear moment to angular momentum characteristic of the nuclei under consideration. Quantitatively, the result of this deviation may be described by a macroscopic polarization vector  $\mathbf{M}$  with components given by Eq. (44) of I,

$$M_x = \frac{M}{(1 + \delta^2)^{\frac{1}{2}}} \cos \omega t, \quad (4a)$$

$$M_y = \mp \frac{M}{(1 + \delta^2)^{\frac{1}{2}}} \sin \omega t, \quad (4b)$$

$$M_z = \frac{M}{(1 + \delta^2)^{\frac{1}{2}}}, \quad (4c)$$

where

$$\delta = (H_0 - H^*)/H_1$$

is the deviation of  $z$  field  $H_0$  from its resonance value  $H^*$  in units of the half-amplitude  $H_1$  of the oscillating  $x$  field. The ambiguous sign in (4b) is to allow for the possibility of either positive or negative values of  $\gamma$ . The quantity  $M$  depends in

a rather involved manner on the nuclear relaxation times and we will only say that, under favorable conditions, it may be expected to be of the order of the equilibrium polarization  $M_0$ ; a precise expression is given in I, Eq. (46).

It is this precessing vector  $\mathbf{M}$  which we wish to observe and either to design or discuss a suitable experimental arrangement for this purpose we need some estimate both of the magnitude of  $\mathbf{M}$  and of the field  $H_1$  needed to produce the precession of  $\mathbf{M}$ . These quantities have the same dimensions and so may be compared directly.

For this purpose we may use numbers taken from the experiments as actually performed, a typical case being the use of protons in water and with a field  $H_0 = 1826$  gauss. With known values of  $\mu$  and  $j$  one finds a saturation magnetic moment density of  $0.6 \times 10^{-6}$  gauss. If now we consider a spherical sample with given moment density, we easily find that the flux linkage through an equatorial circle is equal to that caused by a magnetic field of magnitude  $(8\pi/3)$  times the moment density. Or, in the present case, we can say that the flux linkage through a single equatorial turn about the sphere will be the same as that caused by a uniform field of  $5.1 \times 10^{-6}$  gauss.

In considering possible methods of detecting an oscillating field of this general magnitude, we must not only consider the relative magnitudes of thermal noise power and the power that may be generated by such an oscillating field, but also must compare the magnitude of the field caused by the nuclear moments with the field  $H_1$ .

As remarked in I, the field  $H_1$  should be notably larger than the internuclear fields, which are of order one gauss. Thus, a value of five gauss for  $H_1$  will perhaps be suitable. This specifies the magnitude. As to the phase, we note that, by (2) and (4), the driving field, which is in the  $x$  direction, is in time quadrature with the  $y$  component of the moment to be observed.

Broadly speaking, then, the problem is the detection and measurement of an oscillating field of, say,  $5 \times 10^{-6}$  gauss or less in the presence of a field of the same frequency and of magnitude about 10 gauss, or at least  $2 \times 10^6$  times larger.

To accomplish this we have used an apparatus which may be described with the aid of Fig. 1. This shows a section in the  $yz$  plane, the center

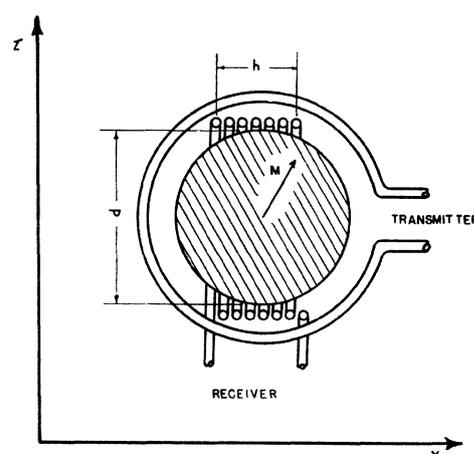


FIG. 1. Schematic diagram of coil arrangement used. A section in the  $yz$  plane shows the spherical sample (cross hatched) surrounded by a receiver coil sensitive to variations in flux in the  $y$  direction and outside this a transmitter coil producing flux in the  $x$  direction. A static field in the  $z$  direction is produced by a magnet not shown.

shaded circle representing the equatorial section of a spherical sample of volume  $\Omega$  containing the nuclei whose total moment  $M\Omega$  is to be observed. A static magnetic field  $H_0$  in the  $z$  direction is produced by an electromagnet (not shown). An oscillating field of peak value  $2H_1$  in the  $x$  direction is produced by current flowing through a "transmitter coil." This coil, though shown as a single turn, in actuality consists of a plurality of turns. In consequence of the oscillating field  $2H_1$  and the static field  $H_0$ , the moment  $M\Omega$  will precess: as a result a variable flux links the "receiver coil," whose axis is in the  $y$  direction, and the resultant voltage which appears at the terminals is led off to a receiver to be measured.

We now return to the problem of the detection of a field of magnitude  $5 \times 10^{-6}$  gauss oscillation at approximately the Larmor frequency, which turns out to be  $7.76 \times 10^6$  cycles/sec., for protons in a field of 1826 gauss. We may consider the problem in two stages: first, how would one measure such a field in the absence of the driving field, and second, what effect does the presence of the driving field have.

As to the first, the obvious procedure is to amplify the voltage induced in the pick-up coil by a suitable amount, whereupon the voltage may be measured by various means—provided it is larger than any spurious voltages that may be present. Practically, it is desirable to increase the

voltage as much as possible by using a multiplicity of turns and by introducing a shunt condenser to induce resonance. In principle, such resonance does not alter the ratio of signal voltage to thermal noise voltage, but in practice it does alter the ratio of signal to observed noise, because both signal and thermal noise are raised relative to the constant amplifier or tube noise.

The apparatus we used had 24 turns on a form of diameter  $d=1.74$  cm and length  $h=0.84$  cm, and had a  $Q$ , with the sample in place, of about 80. The r.m.s. voltage available is then

$$V = \frac{1}{\sqrt{2}} \frac{4\pi M}{(d^2 + h^2)^{\frac{1}{2}}} NQ \times 10^{-8}$$

and, with a sample of volume 1.46 cc this comes out to be  $3.7 \times 10^{-3}$  volt, so that large amounts of amplification are not needed. Also, this may be compared with the thermal noise voltage which, for this coil, is about  $0.7 \times 10^{-6}$  volt in a 3000-cycle-per-sec. band. Thus, an enormous ratio of signal over noise is potentially available. This ratio is independent of the number of turns on the coil, but could be increased for the same sample and coil size by increasing  $Q$  or decreasing the band width.

Two further points must be noted, however.

First, in order to know that the observed amplifier output is caused by the nuclear moments and not by some unknown cause, it is essential that the voltage due to the nuclear moments be varied, or modulated, in some known and controllable manner in which case outputs are real or spurious according as they do or do not correspond to the known modulation.

Second, the magnitude of any spurious signals or "noise" will depend on the frequency band accepted by the resonant pick-up coil and the amplifier which follows. If the noise is of random type, its amplitude will vary with the square root of the band width; if it is of impulse type, the amplitude will vary directly with band width. In any case, it is desirable to reduce the band width as much as possible or convenient, for doing so reduces noise while leaving the signal unaltered.

The straightforward method of reducing the band width is, of course, to increase the sharpness of resonance by reducing the losses as far as may be. Possibilities in this direction are, however,

quite limited. For example, if one attains a  $Q$  of 100, which is quite good for such small coils in the presence of poor dielectric, the band width at 7 mc is  $1.1 \times 10^5$  cycles/sec., or much larger than the minimum set by the requirement that the response time be not inconveniently large. While somewhat larger  $Q$  values may be possible, it is plain that no attainable value will make the band as small as one might desire.

Some improvement might be obtained by making the modulation cyclic, and following the rectifying device which converts the 7-mc signal to a unidirectional one with a filter, or amplifier, sharply tuned to the modulation frequency. The effectiveness of this scheme may be measured by the effective band width, which is of the order  $(\Delta\nu_1 \Delta\nu_2)^{\frac{1}{2}}$  where  $\Delta\nu_1$  and  $\Delta\nu_2$  are the band widths of the circuits before and after the rectifier. Thus reducing  $\Delta\nu_2$  reduces the noise, but not as much as one might hope, since the response time goes with  $1/\Delta\nu_2$ .

The proper way to reduce the band width is by heterodyning the signal down to some lower frequency where a given percentage band width becomes a small absolute band width. This may be done with a detector, and following filter with narrow pass band, if one introduces into the detector an additional signal of constant frequency, usually called the local oscillator signal, and with magnitude large compared to either signal or noise. Then the beats between local oscillator and signal or noise components dominate those between noise components, or between signal and noise components, and the output noise then depends only on  $\Delta\nu_2$ , being quite independent of  $\Delta\nu_1$ . In this way the band width may be reduced by any desired amount, the only limit being set by the response time  $1/\Delta\nu_2$ .

We come now to the question of the effects of the large field  $H_1$  which, it will be remembered, is at least  $10^6$  larger than the field to be detected.

This large background has two effects. First, if even a moderate fraction appears in the receiver, any amplifiers that may be used will saturate long before the signal is of suitable size. Second, and more fundamental, any fluctuation in the background is indistinguishable from a signal and, with such a large ratio of background to signal, such variations can be serious, though they could be, if necessary, controlled.

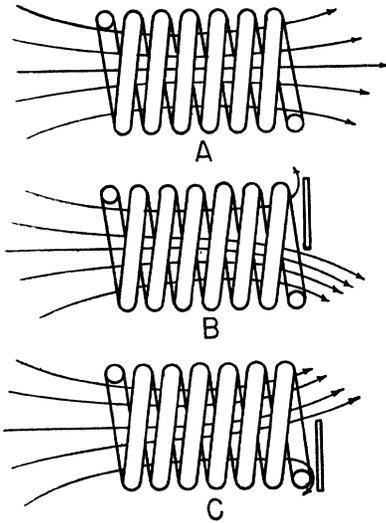


FIG. 2. The drawing (A) shows the flux threading the transmitter coil, while (B) and (C) show how this flux may be "steered" by means of a semicircular copper paddle, so as to link the receiver coil in either the positive or the negative sense.

For these two reasons, we have used a receiver coil which is nearly at right angles to the transmitter coil, so reducing the effect of  $H_1$ , which we call leakage, by a factor  $\sin \epsilon \cong \epsilon$ , where  $\epsilon$  is the deviation of the angle between transmitter and receiver coils from  $\pi/2$ . In this way the leakage of  $H_1$  into the receiver coil may easily be reduced by a factor of  $10^4$  or thereabouts. But a reduction of  $10^6$  or more, while possible, would be difficult, as it would involve adjustment of an angle to  $10^{-6}$  radian, or  $0.2''$ .

In fact, it is not desirable to try for such extreme reduction, since once the leakage has been reduced to a point where it is only, say,  $10^3$  times the signal, it may actually be made to serve an important and useful purpose.

Specifically, we have already pointed out the desirability, from a band width point of view, of heterodyning to some lower frequency, and there is no reason for not choosing this frequency to be zero, in which case the leakage signal, slightly modified, is an ideal source of local oscillator voltage.

The modification needed is in the phase for, as we have seen, the leakage and the signal are  $\pi/2$  out of phase so that, if one adds the leakage to an amount of signal which is varied by the modulation the result, while having nodes that are not

evenly spaced (phase modulation) has a practically constant amplitude, and so, on passage through an ordinary detector, the modulation will not be reproduced. One must, therefore, shift the phase of the leakage by some amount, preferably  $\pi/2$ , whereupon the variable signal will lead to amplitude modulation which is easily detected. The above ideas may also be expressed by means of vector diagrams, in which representation the leakage is a large vector and the signal a small vector at right angles thereto, so that variations in the signal make variations in the vector sum which are quadratic in the signal. If, on the other hand, the phase of the leakage is shifted by  $\pi/2$  so that the vectors are collinear, variations of signal amplitude appear linearly as variations in resultant.

This desired phase shift may be achieved by a device which also serves the purpose of regulating the magnitude of the leakage. More precisely, the device to be described regulates the quadrature component of the leakage: when this is reduced to zero, what remains must be in phase with the signal.

Referring now to Fig. 2A, there is shown, in cross section, the transmitter coil, the receiver coil and the sample being omitted. The flux through the coil will be roughly parallel to the axis or, more exactly, will have symmetry about the axis and will not link any coil whose plane passes through this axis. If now we place a semicircular sheet of conductor across one end of the coil as in Fig. 2B, the currents induced therein will prevent the flux from passing through the sheet. If the lines are going from left to right they would then pass through a plane, at right angles to the paper and containing the axis, in the upward direction. Likewise, if this sheet of conductor, which we call a paddle, be placed as in Fig. 2C the linkage of a coil in the axial plane will be reversed. The change from Fig. 2B to Fig. 2C may be made continuously by mounting the paddle on an axial shaft and rotating same. Thus, by rotating such a shaft either positive or negative flux linkage may be obtained and, by continuity, the desired value of zero must be possible. Any desired sensitivity of adjustment may be had by suitable choice of paddle size.

In this way the quadrature component may be adjusted at will. One might fear that it would be

found that there would be no in-phase component of leakage. Actually this is not found to be true, the reason being that the currents which flow in the paddle are not  $\pi$  out of phase with the currents in the transmitter coil, because of losses in the paddle, and so have a component in phase with the signal.

It remains only to describe the methods of modulation and presentation.

To cause the signal to vary in strength one might vary either the  $z$  magnetic field  $H_0$  or the frequency. The former seemed the easier and was adopted for the experiments here described, the field  $H_0$  being varied cyclically about a value  $H_{dc}$ . The modulation frequency of 60 cycles/sec. was chosen as being low enough to avoid excessive band width and high enough for the persistence of vision needed for the cathode-ray tube presentation used. Within limits set by these factors a considerable range of frequencies is possible: of these 60 cycles/sec. has the additional advantage that any spurious hum pick-up appears as a recognizable distortion of the final pattern rather than as a blurring.

Presentation was on a cathode-ray tube with horizontal plates giving a deflection proportional to the variation in  $H_0$  and the vertical plates giving a deflection proportional to the signal which in turn depends on the  $y$  component of the nuclear magnetic moment. Thus one observes on the screen a plot of  $M_y$  vs.  $H_0$ , the center of the screen corresponding to the field  $H_{dc}$ .

We may summarize by giving, in Fig. 3, a block diagram of the complete apparatus. Here the spherical sample is immersed in a field  $H_{dc} + H_{ac} \cos 377t$  produced by a magnet, not shown. The nuclear moments oriented by this field are caused to precess by a driving field  $H_x$  produced by current from the box labeled transmitter. The precessing moments induce voltages in the receiver coil. These voltages, which vary in

amplitude at a 60 c/sec. rate because of the variations in field  $H_0$ , are amplified along with stronger constant amplitude leakage signals. The leakage and the varying voltages due to precessing nuclei are mixed in the detector, the output of which then contains pulsating unidirectional current, the steady component due to leakage and the variations corresponding to the desired signal. The d.c. is removed by the blocking condensers in the following amplifier which increases the signal voltages to a magnitude suitable for operation of the cathode-ray tube.

#### APPARATUS

We now describe in detail the equipment constituting the various blocks in the above diagram.

The steady magnetic field  $H_{dc}$  is supplied by a lecture-demonstration magnet which easily produces the necessary fields of a few thousand gauss. The poles are 3 inches in diameter and these are provided with laminated extensions of transformer sheet which are  $3\frac{1}{2}$  inches  $\times$   $3\frac{1}{2}$  inches and 1 inch thick. The spacing between these laminated extensions is  $1\frac{1}{2}$  inches and within the central volume of 2 cc, occupied by the sample, the field was found, by flip coil measurements, to be uniform to within 2 gauss. Since variations in field of order  $H_1 = 5$  gauss could be tolerated without undue broadening of the resonance peak, this uniformity is satisfactory.

The 60 c/sec. modulation of the field is provided by current flowing through two coils of about Helmholtz proportions, placed between the laminated pole faces and carrying 60 c/sec. current. The magnitude of this current can be regulated by means of a variac to give values of  $H_{ac}$  between zero and 50 gauss. The same current which passes through the coils passes also through a resistor, and the resulting voltage drop actuates the horizontal sweep of the oscilloscope.

As to the transmitter, the main requirement in addition to ability to deliver enough power to maintain the field  $H_1$ , is a very high order of output amplitude stability. This requirement arises because variations in leakage are indistinguishable from signal and because even the smallest leakage is large compared to the signal. For example, if the nuclear moment per unit

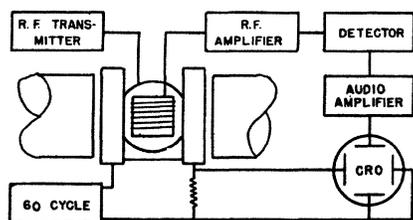


FIG. 3. Block diagram of apparatus.

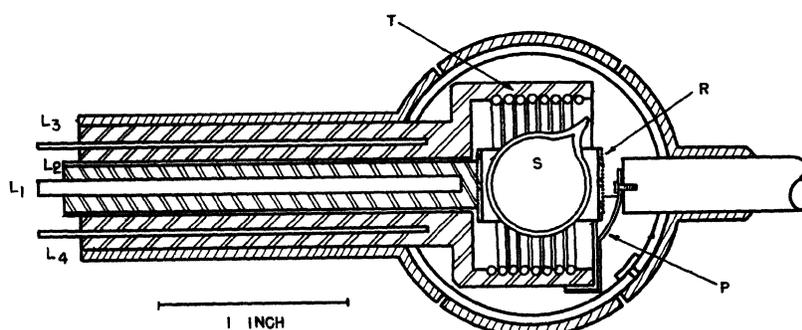


FIG. 4. Scale drawing of an  $xy$  section of the r-f head. The spherical sample  $S$  is surrounded by a receiver coil  $R$ , which is in turn surrounded by a transmitter coil  $T$ , the whole being encased in a shield. A rotably mounted paddle  $P$  is used to steer the transmitter flux. Leads to the receiver coil are the coaxial leads  $L_1L_2$  while the transmitter leads are  $L_3$  and  $L_4$ . The outer shield is split to avoid 60-cycle eddy currents.

volume is  $10^{-7}$  times  $H_1$ , as it might be in a typical case, then even if the leakage is reduced to, say,  $10^{-3}$  of  $H_1$ , a variation in transmitter output by a part in  $10^4$  will cause a fluctuation equal to the signal.

The power required to maintain the field  $H_1$  is of the order 1 watt and this, together with considerable excess to allow for imperfect impedance matching, etc., is easily supplied by an 815. The stability is achieved by deriving both filament and plate power from batteries. Magnetic regulators in the primary of an ordinary supply were tried and found worthless because of slow response. A carefully engineered and tested vacuum-tube regulator might do, but batteries were adopted as quicker and absolutely reliable.

The transmitter and receiver coils are best described by the drawing of Fig. 4, which shows the coils and surrounding shield which we may call the r-f head. The transmitter coil consists of seven turns of mean diameter  $\frac{7}{8}$ " and length  $\frac{1}{2}$ ", wound inside a threaded polystyrene shell. Inside the transmitter coil is placed the receiver coil of 24 turns,  $\frac{9}{16}$ " in diameter and  $\frac{5}{16}$ " long, wound on the outside of a thin threaded polystyrene form. Inside this, in turn, is the sample, contained in a glass bulb  $\frac{1}{2}$  in. in diameter. The design aims at the greatest mechanical rigidity and damping possible, in an effort to avoid vibrations which, by varying the coupling between transmitter and receiver, vary the leakage and so introduce microphonics. Such microphonics constitute the biggest experimental difficulty with the equipment here described.

Transmission lines a few inches long lead to a brass box about 4 inches by 8 inches by  $8\frac{1}{2}$  inches, which is divided in two by a horizontal partition. The lower portion contains tuning condensers to resonate the transmitter coil; the upper contains a similar condenser for the receiver and also the detector and first audio stage of the receiver, together with suitable batteries for same.

The receiver differs from the block diagram in that the r-f amplifier there shown is omitted, the receiver coil working directly into a diode detector. This has the disadvantage of a very considerable loss in potential signal/noise ratio, but in view of the large signal available from protons it was decided to sacrifice this in the interests of simplicity. This simplicity appears in two ways: First, one replaces an r-f amplifier by a simpler audio stage, and second, whereas a volt or less might saturate an r-f stage, the diode will not saturate. This point is very important in tuning up, for at the start the leakage voltage is usually 100 volts, or more, and it is only after considerable adjustment that this can be reduced to about 0.1 volt which is usually used in operation. The diode detector is conventional as is the first audio stage which acts mainly as an inverter and impedance changer, giving push-pull output at low impedance level. This low impedance output is carried to the main amplifier by a few feet of cable.

The requirements on this amplifier are that it have a gain of a few thousand and pass all significant signal components without appreciable amplitude or phase distortion. The fre-

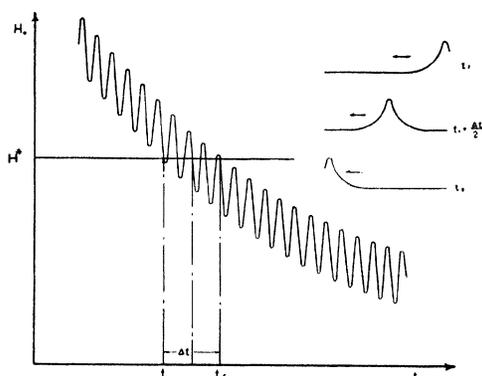


FIG. 5. Schematic representation of the modulated  $z$  component  $H_0$  of the magnetic field in its dependence upon time. As the magnet current decreases, the resonance field  $H^*$  is first reached at the initial time  $t_i$  and last at the final time  $t_f$ . During the interval  $\Delta t$  a positive signal is observed to travel across the oscillograph screen as indicated by the arrows on the traces, sketched for three different times at the beginning, the middle, and the end of  $\Delta t$ .

quencies involved are the modulation frequency of 60 c.p.s. and various harmonics thereof. With  $2H_1$  of, say, 10 gauss and  $\Delta H$  of 100 gauss, the first ten harmonics will be of about equal strength and from there on up the strengths will decrease rapidly. About fifty harmonics should then be ample and the amplifier must then pass frequencies between 60 and 3000 cycles/sec. Actually the amplitude response must be practically flat to a considerably lower frequency, say, 6 cycles/sec., if phase shifts in the lower harmonics are not to cause undesirable pedestal effects.

These requirements were met by a three-stage amplifier, using push-pull twin triodes (7F7) throughout. The use of push-pull amplification eliminates cathode bypass condensers and, more important, cancels the otherwise very annoying disturbances due to power supply variation. Likewise, screen by-passes are not needed and the Miller effect is not bothersome because of the rather low value of high frequency cut-off. The amplifier was tested on 60 c/sec. square waves, which it passes without distortion.

Although frequency response, as specified above, is needed to give a completely undistorted pattern on the oscilloscope, it is found in practice that the amount of pedestal effect introduced by raising the low frequency cut-off to 60 or 120 cycles is not objectionable, and the reduction in

low frequency disturbances obtained by raising the low frequency cut-off is often a convenience.

Finally, the output of this amplifier actuates the vertical sweep of a Dumont 208 oscillograph and thereby traces a curve of  $M_y$  vs.  $H_0$  suitable for visual observation.

## RESULTS

Using the method and apparatus described above, we have so far investigated nuclear induction of protons only. The advantage of working with protons is twofold. In the first place they have of all known nuclei the highest gyromagnetic ratio  $\gamma$  so that moderate fields are sufficient to bring the resonance frequency into the convenient frequency range of a few megacycles. In the second place there is a great choice of compounds and solutions containing hydrogen which facilitates variation of the conditions of observation, particularly with respect to the relaxation times.

Our first experiments were carried out with water contained in small spherical glass bulbs which could be sealed off. The very first signal was observed with a sample of only 100 milligrams, but in all later experiments the amount was increased to about 1 gram, the glass bulbs being increased to a volume of about 1 cc. These samples were placed into the receiver coil and, after mounting the shields and the a.c. coils, providing the field modulation, were moved into the center of the magnet gap. With proper tuning and adjustment of the apparatus we could then observe the proton signal on the oscillograph screen as the current in the magnet was set to a

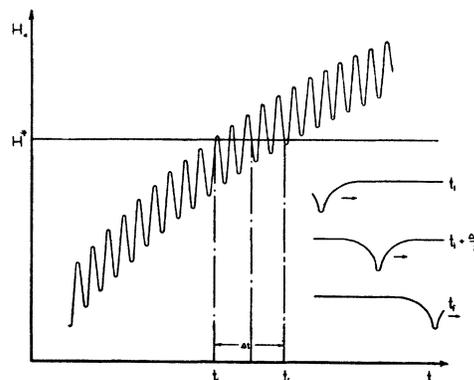


FIG. 6. Time dependence of  $H_0$  as the magnet current increases. A negative signal travels across the screen as indicated by the arrows on the three sketched traces.

value such that the resonance field was contained within the limits of variation determined by the amplitude of the modulating field.

The behavior of the observed signal is determined by various factors, particularly the ratio of the relaxation time to three other time constants which enter into our experiment. The smallest is the time taken to pass through the resonance width which is usually a small fraction of 1/120 sec. The next time of importance is the time between successive transits through resonance, of the order of 1/120 sec. Finally there is the time during which  $H_{dc}$  is varied by an amount comparable to  $H_{ac}$ ; this time can be chosen at will to be anywhere between the time constant of the magnet of the order of one second and many minutes. The following experiments cover various orders of magnitude of the relaxation time relative to the above-mentioned times.

The easiest and most striking visual observation of the protons in water was obtained by first raising the current in the magnet considerably above the value necessary for resonance conditions and then turning it off. This causes the field of the magnet to decrease exponentially with an appreciable time constant, the resonance field entering and leaving the modulation range during a time  $\Delta t$  of about half a second. The variation of the  $z$  component  $H_0$  of the field with time is schematically plotted in Fig. 5. The signal was

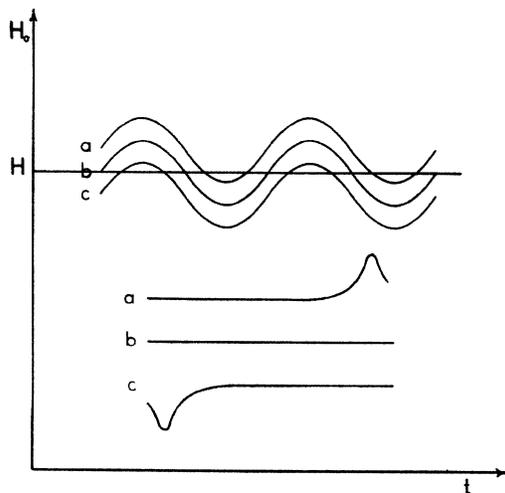


FIG. 7. Time dependence of  $H_0$  with constant magnet current. The a.c. modulation is superimposed upon a d.c. value which in case *a* is above, in case *b* at, and in case *c* below the resonant field  $H^*$ . The three sketched traces represent the corresponding oscillograms.

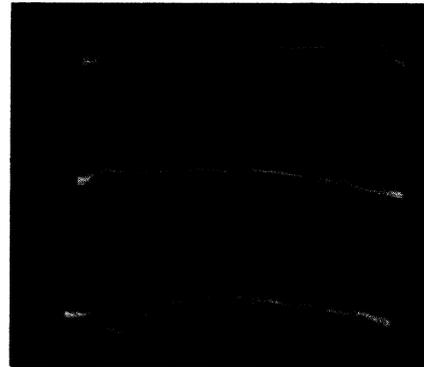


FIG. 8. Photographic record of the proton signal from water. The three traces from top to bottom correspond to the situation *a*, *b*, *c* of Fig. 7.

here observed to appear on the right side of the oscillogram at the initial time  $t_i$ , travel across the screen during the time  $\Delta t$ , and to disappear on the left side at the final time  $t_f$  as indicated on Fig. 5. The time dependence of  $H_0$  and the corresponding observed oscillograms in the inverse process of turning the magnet current on are schematically indicated in Fig. 6.

The most interesting feature to be observed lies in the fact that in the case of Fig. 5, where the field is decreasing, the observed signal voltage is positive while it is negative in the case of Fig. 6 with increasing field. This remarkable "memory" of the proton induction is in perfect agreement with the formulae (4) and with the expression for  $M$ , given in I, Eq. (46). It indicates that the relaxation time  $T_1$  is long compared to the duration  $\Delta t$  of the observation; the sign of  $M$  is determined by the sign of  $\delta$  in the past, which is predominantly positive for decreasing and negative for increasing fields.

It must be noted that, strictly speaking, one cannot directly deduce from the sign of the observed voltage the sign of the signal which, as was pointed out in I, depends also upon the sign of the proton moment. All that can be concluded is that an inversion of the observed (rectified) signal means a reversal of the actual (radiofrequency) signal with respect to the in-phase leakage voltage. To ascertain the sign of the proton moment would require a determination of the sign of the in-phase leakage voltage which we have not carried out in view of the fact that the proton moment is already known to be positive.

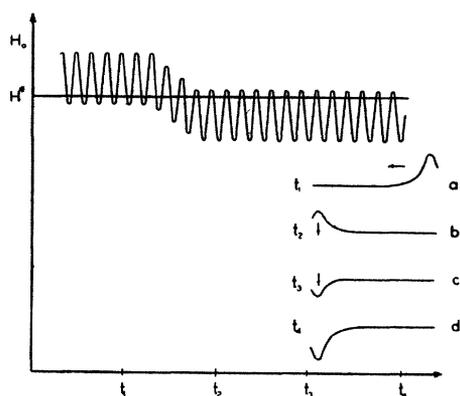


FIG. 9. Time dependence of  $H_0$  with a d.c. value of the field being above the resonant field  $H^*$  for  $t < t_1$ , decreasing between  $t_1$  and  $t_2$  and being below  $H^*$  for  $t > t_2$ . The sketched traces  $a$ ,  $b$ ,  $c$ ,  $d$  represent oscillograms at four different times, the arrows indicating the initial shift and subsequent reversal of the signal.

Another method of observing the proton signal in water is indicated in Fig. 7. The current in the magnet, and so  $H_{dc}$ , is here kept constant. With the relaxation time  $T_1$  long compared to  $1/60$  second, the signal voltage is, according to I, Eq. (46), essentially determined by the time average of  $\delta$  which is positive in case  $a$ , zero in case  $b$ , and negative in case  $c$ . A photographic record of the three oscillograms is shown on Fig. 8.

The methods of observation, indicated in Figs. 5-7, allow only a conclusion as to the lower limit of the relaxation time. Thus the behavior of the signal under the conditions of Fig. 7 merely indicates that the relaxation time is long compared to  $1/60$  second; the fact that with decreasing or increasing current, as in Figs. 5 and 6, the signal does not reverse its sign while traveling across the oscillograph screen during about  $\frac{1}{2}$  second sets the lower limit of the relaxation time higher, namely to a value large compared to  $\frac{1}{2}$  second. It was observed, on the other hand, that if the current was first decreased, as in Fig. 5, and then made to increase so that resonance conditions, as in Fig. 6, were again reached after about one minute, there was no "memory" retained of the previous decrease. This allows at least the conclusion that the relaxation time is short compared to a minute, and in order to establish its actual value, to be expected somewhere between  $\frac{1}{2}$  second and one minute, the method of observation, indicated in Fig. 9 was chosen: Starting at a time  $t_1$ , with  $H_{dc}$  held for a considerable previous

time above the resonance field  $H^*$  a positive signal was observed on the right side of the oscillogram, similar to the case  $a$  of Fig. 7 and as presented on trace  $a$  of Fig. 8. Thereupon the field was quickly (i.e., during about one second) lowered to a value sufficiently below resonance to make the signal appear on the left side of the oscillogram and then was held fixed at this new value. As was to be expected from the analogous situation of Fig. 5, the signal was originally still positive. However, during the following few seconds it was observed to decrease in magnitude, then to disappear and thereupon to grow again with negative values until after several seconds it had reached its full negative value, corresponding to the case  $c$  of Fig. 7 and as presented on trace  $c$  of Fig. 8.

This extraordinary reversal of the signal under fixed external conditions represents actually a direct visual observation of the gradual adjustment of the proton spin-orientation to the changed situation caused by the previous change of the magnet current. The fact that it takes place during a time interval of several seconds evidently indicates the relaxation time, likewise, to be of the order of a few seconds. A photographic record of the process is reproduced on Fig. 10. The top trace  $a$  is taken at an instant (and with an exposure of slightly over  $1/60$  second), corresponding to the time  $t_1$  of Fig. 9.



FIG. 10. Photographic record of the proton signal in water. The four traces from top to bottom correspond to the times  $t_1$ ,  $t_2$ ,  $t_3$ ,  $t_4$  of Fig. 9. In the text they are referred to as  $a$ ,  $b$ ,  $c$ ,  $d$ , respectively.

The following three traces represent snapshots taken during the next 15 seconds at regular 5-second intervals and clearly show on trace *b* the decrease and on traces *c* and *d* the reversal of the signal. The fact that on traces *a*, *b*, *c*, and (slightly) also on trace *d* there appear two separated signals on top of each other is caused by stray 60-cycle pick-up which has the same frequency as the modulation and, appearing on top of the actual proton signal manifests itself in a separation of the forth- and back-sweep, recorded during the exposure of the camera.

It was most surprising thus to establish the proton relaxation time in water to be of the order of a few seconds, although it must be admitted that it is difficult, as pointed out in I, to give a reliable theoretical estimate. Whereas such an estimate can be given for a gas and, to some extent, also, for a crystal, there is not enough known about the molecular motion in liquids to predict more than a crude order of magnitude. Treating the liquid either as a highly compressed gas or as a crystal with thermal amplitudes of the molecules, comparable to the lattice constants one would expect the relaxation time to be of the order of a few hours rather than of a few seconds.

We must point out here that the "relaxation time," as observed in our experiments, does not necessarily represent the usual (and in I, referred to as the "longitudinal") paramagnetic relaxation time  $T_1$  but that it represents rather an "effective" relaxation time, which can be influenced by the possibly different transversal relaxation time  $T_2$ , introduced in I. It will require a good deal more experimentation and observation under various conditions to separate clearly the effects of  $T_1$  and  $T_2$  and, with the use of Eq. (46) of I, to ascertain their values separately. This point, however, relates to the quantitative rather than to the qualitative interpretation of our results and is by no means sufficient to explain the extraordinary difference in magnitude between the observed effective and the theoretically expected paramagnetic relaxation time.

We suspected the origin of this discrepancy to be caused by slight impurities and particularly to oxygen dissolved in water. Because of the magnetic moment of the oxygen molecules, acting as catalysts, it would actually take only one molecule of  $O_2$  in about a thousand molecules of  $H_2O$  to

explain relaxation times of the order of a few seconds. In order to verify this hypothesis we had one of our water samples purified by distillation in a vacuum\* with a final partial pressure of oxygen of probably no more than  $10^{-4}$  mm. While with the previous unpurified samples the reversal of the proton signal was essentially completed after 4 to 5 seconds, it took with the purified sample about 15 seconds for completion of the reversal. There is thus a noticeable effect of shortened relaxation times by impurities but it is by no means sufficient to explain their abnormal shortness. We can, of course, not discard the possibility that even after distillation there remained impurities in the water (originating, e.g., from material adhering to the glass walls) of sufficient amount and catalytic effectiveness to determine mainly the observed relaxation time. However, it does not seem very probable to us that this is the case, since in one of our experiments mineral oil was used instead of water. It exhibited a relaxation time of the same order of magnitude, while the entirely different chemical nature should be expected to result in a different composition of impurities. Nevertheless there may be an accidental coincidence and more experiments will be necessary to clarify the role of impurities.

Another experiment of interest was carried out with ice. The water was frozen in a small container and placed into the transmitter-receiver assembly. No noticeable signal was observed while the water was still frozen but the signal started to show up with the beginning of the melting process. We interpret this result as indicating a very long relaxation time in ice, since it was shown in I, Section 4, that the magnitude of the signal decreases indefinitely for sufficiently increasing  $T_1$ .

It seems reasonable, from theoretical considerations, that the relaxation time in a solid should be considerably longer than in a liquid and in this respect there is nothing remarkable in the behavior of ice. It was the more surprising to find another solid, namely paraffin, to behave in an entirely different manner. With the same method of observation as indicated in Fig. 5 and 6 for

\* We wish to thank Dr. R. A. Ogg for kindly preparing the sample for us and for valuable discussions relating to the chemical aspect of our experiments.

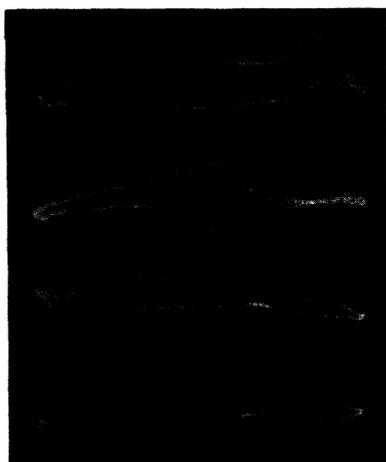


FIG. 11. Photographic record of the proton signal in paraffin. The four traces from top to bottom are in the text referred to as *a*, *b*, *c*, and *d*.

water it was found that even during the  $\frac{1}{2}$  second which it took the signal to travel across the screen, it showed instantaneous reversal after passing the midpoint and that there was no observable dependence of the aspect of the signal upon the previous values of  $H_{dc}$ . While this indicates already a relaxation time considerably shorter than that of water, its actual value could be directly ascertained by observation under conditions equal to those of Fig. 7. The photographic record is shown in Fig. 11 with the traces *a*, *b*, *c* referring to the same values of  $H_0$  as the corresponding ones on Fig. 8. A fourth "zero" trace *d* is shown on the plate where the resonance field  $H^*$  was well outside the sweep range so that there appears no signal. As on Fig. 10, there appears a spurious signal which slightly separates the forth and back sweep on the oscillogram to make the trace *d* look like the "infinity," sign of mathematics. This accidental separation of the two sweeps is actually quite desirable in this case since, contrary to the case of water on Fig. 8 where they coincide and show the complete identity of the signals on the two traces, there is here a marked difference. On trace *a*, where the resonance occurs near the minimum of  $H_0$ , both signals are still positive, the signal on the back sweep (below) being, however, considerably smaller than that on the forth sweep (above). The explanation is obviously that on the forth sweep the previous value of  $\delta$  during almost a



FIG. 12. Photographic record of the proton signal in a concentrated solution of  $\text{Fe}(\text{NO}_3)_3$  in water. The four traces from top to bottom are in the text referred to as *a*, *b*, *c*, *d*.

complete cycle was positive but that for the back sweep it is no more the average value of  $\delta$  as in the case of water, which determines its magnitude, since this would be the same for the two sweeps. Instead the short time interval of about  $1/240$  second during which  $\delta$  is negative until returning to zero, suffices, not to make the back signal negative, but at least to diminish it considerably. The identical behavior in reverse is shown on trace *c* where resonance occurs near the maximum of  $H_0$  with both signals negative and the one on the back sweep (above) being smaller in magnitude than that on the forth sweep (below). With  $H_{dc} = H^*$  and the signal therefore appearing at the center of the oscillogram, the time interval of  $1/120$  second is sufficient for complete reversal of the signal, as shown on trace *b*.

This leads to the conclusion that, contrary to our expectations, the relaxation time in paraffin is only of the order of  $1/100$  second. For a solid this is indeed extraordinarily short and only an unsuspectedly large amount of impurities can explain it, provided that the true explanation will not be found in a yet unknown and entirely different mechanism.

The results of a last set of experiments are shown on Fig. 12. Here we were dealing with a concentrated solution of  $\text{Fe}(\text{NO}_3)_3$  in water in

order to obtain a case in which, because of the atomic moments of the Fe ions, the relaxation time is short compared to the time required to pass through resonance conditions. We obtain thus the case of "slow passage," discussed in I, Section 5. The shape of the signal is here in complete agreement with the theoretical formula, I (53), having a zero at resonance and an up- and down-swing for positive and negative values of  $\delta$ , respectively. Except for their position, there is no difference in the signals received on the three traces  $a$ ,  $b$ ,  $c$  which pertain to the corresponding values of  $H_{dc}$ , represented in Fig. 6. A "zero" trace  $d$  is again added, showing the slight separation of forth- and back-sweep.

With the time, required to sweep through the signal of about 1/600 second we estimate the relaxation time to be here of the order of  $10^{-4}$  to  $10^{-5}$  sec. Other data, showing the dependence of the relaxation time upon the concentration of the paramagnetic salt will be published shortly.

The shape of the signal obtained with  $\text{Fe}(\text{NO}_3)_3$  solutions makes it particularly easy to locate the resonance value of  $H_{dc}$  by setting the magnet current to such a value that the zero point of the signal is located at the exact center of the oscillogram. With the whole resonance width amounting to only about 1 percent of the total field, this setting can be easily adjusted to within the order of one per mille.

We have verified that the value of the resonance field determined in this manner agrees with the gyromagnetic ratio for protons determined by Kellogg, Rabi, Ramsey, and Zacharias.\* After determining the resonance frequency and without altering the magnet current, the modulating a.c. field was turned off, the transmitter-receiver assembly removed and a carefully measured flip coil brought to the original position of the sample between the pole pieces in order to determine the value of the resonant field  $H^*$ . With a frequency  $\nu = 7.765 \times 10^6$  sec. $^{-1}$  it was found that the resonance field had the value  $H^* = 1826$  gauss which leads to a value of the gyromagnetic ratio

$$\gamma = 2\pi \frac{7.765 \times 10^6}{1826} = 2.672 \times 10^4.$$

The agreement within one-quarter of a percent with the value  $\gamma = 2.665 \times 10^4$ , obtained with molecular beams, must be considered accidental since our field measurement can only claim an accuracy of about 1 percent. We have also verified, although with somewhat less accuracy, that the ratio  $\nu/H^*$  for the resonance signal, obtained from water, remains the same for  $\nu = 7.8 \times 10^6$ ,  $\nu = 8.8 \times 10^6$ , and  $\nu = 10.7 \times 10^6$ .

\* J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, Phys. Rev. **56**, 728 (1939).

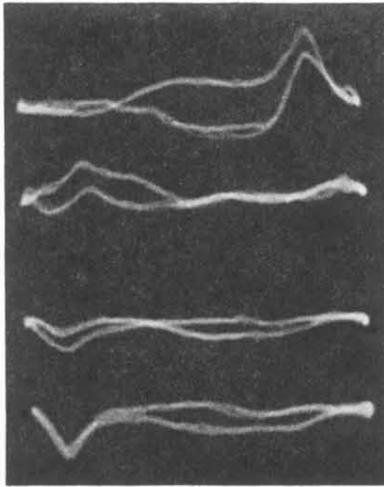


FIG. 10. Photographic record of the proton signal in water. The four traces from top to bottom correspond to the times  $t_1$ ,  $t_2$ ,  $t_3$ ,  $t_4$  of Fig. 9. In the text they are referred to as  $a$ ,  $b$ ,  $c$ ,  $d$ , respectively.

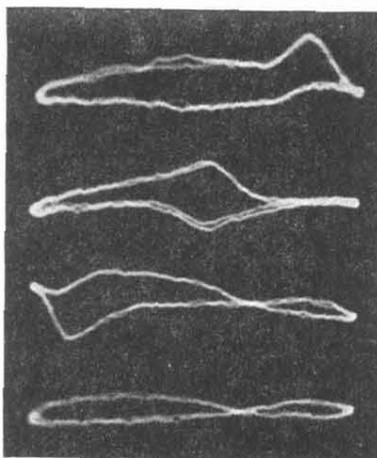


FIG. 11. Photographic record of the proton signal in paraffin. The four traces from top to bottom are in the text referred to as *a*, *b*, *c*, and *d*.

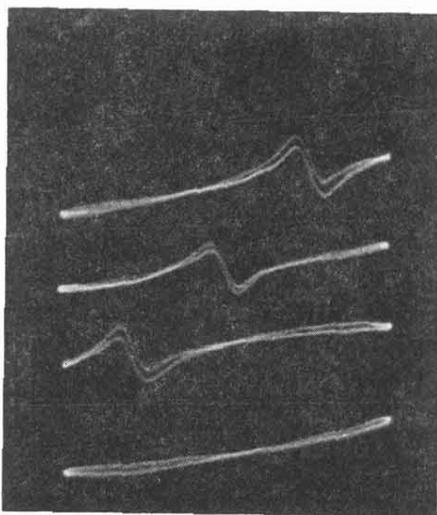


FIG. 12. Photographic record of the proton signal in a concentrated solution of  $\text{Fe}(\text{NO}_3)_3$  in water. The four traces from top to bottom are in the text referred to as *a*, *b*, *c*, *d*.

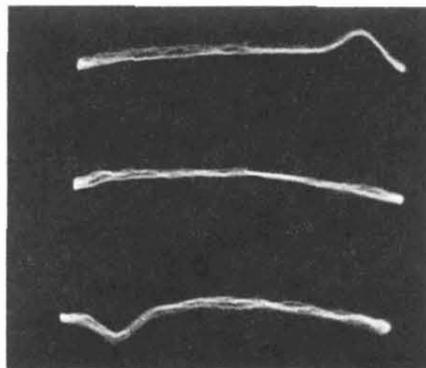


FIG. 8. Photographic record of the proton signal from water. The three traces from top to bottom correspond to the situation *a*, *b*, *c* of Fig. 7.