NUCLEAR MAGNETIC RESONANCE
by D. J. KROON.

The phenomenon of nuclear magnetic resonance in solids and liquids yields absorption spectra from which valuable information on their structures can be obtained. The article below first gives a simple exposition of the theory, and then describes in more detail the equipment required and a few applications. The latter illustrate the usefulness of the method both for pure scientific research and for routine investigations in various industries.

Introduction

Amongst the most recent tools in the investigation of condensed phases (solids and liquids) are the methods of measurement that depend on the absorption of electromagnetic energy at specific wavelengths in the metre and centimetre regions. According to the mechanism causing the absorption, the methods can be divided into three groups: paramagnetic resonance, nuclear magnetic resonance and cyclotron resonance.

In paramagnetic and nuclear magnetic resonance the absorption is caused by the presence in the substance of elementary magnets, i.e. the “spins” of electrons and atomic nuclei which, in the presence of a constant external magnetic field, are subjected to an alternating magnetic field. Cyclotron resonance occurs when more or less free electrons (e.g. in semiconductors), in the presence of a constant external magnetic field, are subjected to an alternating electric field. In this article we shall be concerned only with nuclear magnetic resonance. The related effect of paramagnetic resonance was described in an article published some time ago in this journal 1), to which we shall refer when occasion arises. An appendix to the present article deals in some detail with the points of difference between paramagnetic and nuclear magnetic resonance.

As mentioned, nuclear magnetic resonance occurs when atomic nuclei exhibit a spin, that is to say, they have a net angular momentum and magnetic moment. This is so with many kinds of nuclei, in principle in all cases where the number of neutrons and the number of protons in the nucleus are not both even. Familiar examples of nuclei that show a readily measurable effect, i.e. a marked absorption, are $^{19}$F, $^{23}$Na, $^{27}$Al and $^{31}$P, but most especially $^1$H, the hydrogen nucleus or proton.

The information that nuclear magnetic resonance can provide is of various kinds. Hydrogen atoms are present in many inorganic solids (e.g. in molecules of water of crystallization) and in nearly all organic molecules. The form in which the hydrogen nuclei are present has an influence on the resonance spectrum, i.e. the spectral distribution of the measured absorption. In an organic liquid, for example, each kind of molecule containing hydrogen shows a characteristic line spectrum, which can therefore serve for identifying the molecule. In this way it is possible to analyse mixtures of organic compounds. Nuclear magnetic resonance equipment is for this reason regularly used for routine analyses in the petroleum and oil-refining industries and the plastics industry. In solids the resonance frequency of the H nucleus is very broad. From the spectral distribution of the absorption here, one can draw conclusions regarding the ordering of H ions and other ions in the crystal and also regarding the motion of electrons and ions, diffusion phenomena, and so on.

An earlier article in this Review explained how nuclear magnetic resonance can also be used for the accurate measurement of magnetic fields 2). We shall touch on this application when describing the equipment.

In the following pages we shall first give a simple theory of the phenomenon of nuclear magnetic resonance. After describing the measuring equipment we shall consider, by way of illustration, some examples of problems that have been studied by the method of nuclear magnetic resonance. When dealing with the equipment we shall distinguish between measurements on solids and on liquids. Owing to the different nature of their spectra, these two states of aggregation call for different techniques of measurement.

For the determination of crystal structures the well-established methods of X-ray diffraction and infra-red absorption can also be used. It is important to note, however,

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that these methods are not so suitable when it is a matter of detecting and localizing hydrogen atoms.

X-ray diffraction depends on the scattering of X-rays by the atoms or ions of which a crystal lattice is built up. This scattering decreases rapidly the lower the atomic number of the atom or ion. Scattering by H ions is so weak that information on these ions can be obtained from X-ray-diffraction measurements only by indirect means. The related method of neutron diffraction is better in this respect, and in fact has proved very useful 3). It can only be adopted, however, in laboratories associated with a suitable nuclear reactor. Moreover, in these investigations it is often desirable to replace the hydrogen ions (protons) by ions of heavy hydrogen (deuterons), which of course is only practicable in special cases 4).

The infra-red absorption of hydrogen atoms bound to oxygen (OH vibrations) is readily measurable. The frequency of these vibrations depends markedly on the surroundings of the OH group in the lattice, and it is frequently possible to deduce the configurations in which the OH group occurs in the crystal. The interpretation of the measurements, however, is very complicated and the information obtained is generally insufficient for a complete determination of the structure. Furthermore, the sample under measurement is required to be transparent to some extent, which often calls for the use of special techniques.

The method of nuclear magnetic resonance is thus a useful complement to the older methods of structure determination.

Historical note

As long ago as 1936 the Dutch physicist C. J. Gorter predicted the possibility that electromagnetic waves would be absorbed in a solid through the agency of the atomic nuclei if these were subjected to an external magnetic field. His experiments at the time produced no results. It later appeared that the substances on which the experiments were done happened to show only a very small effect, and this was the main reason for the failure of the experiment. Some years later, thanks to the advances in high-frequency techniques, the physicists F. Bloch and E. M. Purcell, working independently and with different methods of measurement, were able to confirm Gorter's theory. In 1952 both these American workers were awarded the Nobel prize for physics.

Concise formulation of the theory of nuclear magnetic resonance

In general an atomic nucleus possesses, apart from mass and electric charge, an angular momentum and a magnetic moment. In the classical model, the atomic nucleus is imagined to behave like a rapidly spinning magnetic top, the magnetization being in the direction of the axis of rotation. Quantum-mechanical considerations require that if the nucleus be subjected to a constant external magnetic field, the axis of rotation of the top, which precesses about the field direction, can assume only certain discrete orientations with respect to the direction of the magnetic field. The number of possible orientations depends on the magnitude of the angular momentum. For hydrogen nuclei (protons) there are two possible orientations, viz. in the direction of the field and opposite thereto. Other nuclei have two or more possible orientations (fluorine 2, sodium 4, bismuth 10).

The energy of the nuclear magnet in the magnetic field is:

\[ E = \mu B \cos \theta, \]

where \( \mu \) is the magnitude of the magnetic moment, \( B \) the field strength (induction) and \( \theta \) the angle between the elementary magnet and the external field (fig. 1). The possible values of \( \cos \theta \) are given by the formula:

\[ \cos \theta = \frac{m_I}{\sqrt{I(I + 1)}}, \]

Fig. 1. Magnetic dipole (moment \( \mu \)) in a magnetic field \( B \).

where \( I \), the spin quantum number of the nucleus, is a multiple of \( \frac{1}{2} \), and \( m_I \) can assume a number \((2I + 1)\) of discrete values, each differing by 1, the extremes being \( I \) and \(-I\). The energy \( E \) can also be written in the form:

\[ E = \mu_s B \frac{m_I}{I}, \]

where \( \mu_s = \mu \sqrt{I(I + 1)} \) represents the largest possible projection of the magnetic moment \( \mu \) on the axis of the field. The magnetic moment \( \mu \) is given by:

\[ \mu = g \sqrt{I(I + 1)} \frac{e \hbar}{4 \pi m_p}, \ldots \ldots (1) \]

where \( e \) and \( m_p \) represent respectively the charge and mass of the proton, and \( g \) is a numerical constant.

that differs according to the type of nucleus (in general $g$ is between 0.1 and 10).

The spin quantum number for hydrogen nuclei is $I = \frac{1}{2}$. There are thus, as remarked, only two states possible. The energy difference between these states is

$$\Delta E = 2\mu_2 B.$$ (2)

In an external field $B = 0.5$ Wb/m$^2$ [5000 gauss] this energy difference is of the order of $10^{-26}$ J ($10^{-7}$ electronvolt).

If the nucleus is subjected simultaneously to a constant magnetic field and an alternating magnetic field at right angles thereto, there is a possibility that the atomic nucleus will change from the one state to the other, whereby an amount of energy equal to the difference $\Delta E$ will be absorbed from the alternating field or given up to it. The condition for the occurrence of such transitions is that the frequency $f$ of the alternating field should satisfy:

$$f = \frac{\Delta E}{h}, \quad \ldots \ldots \ldots \quad (3)$$

where $h$ is Planck's constant ($h = 6.62 \times 10^{-34}$ Js).

Eliminating $\Delta E$ from the expressions (2) and (3) gives the condition for resonance absorption as

$$f = \frac{2\mu_2}{h} B, \quad \ldots \ldots \ldots \quad (4a)$$

or, after substitution of $\mu_2$ (from (1)) and putting $I = \frac{1}{2}$:

$$f = g \frac{e}{4 \pi m_p} B. \quad \ldots \ldots \ldots \quad (4b)$$

For hydrogen nuclei $\mu_2$ is $1.4 \times 10^{-26}$ A.m$^2$. In a field of $B = 0.5$ Wb/m$^2$, as mentioned above, we thus have $f = 21.3$ Mc/s.

The procedure for observing the absorption is basically as follows. A sample of the substance having sufficient nuclei of the type under investigation is introduced into a coil which is connected to a weak high-frequency source of roughly the resonance frequency $f_0$. The coil is placed between the poles of a magnet and the magnetic field is slowly varied. When the magnetic field $B_0$ reaches the value given by (4a) — for the frequency $f_0$ — resonance occurs, giving rise to a slight energy absorption which results in a change in the $Q$ of the coil. By including the latter in a suitable circuit, e.g. a bridge circuit, the change in the $Q$ can be measured and recorded as a function of $B$, to give the magnetic absorption spectrum. The effect of relaxation phenomena on the absorption will be touched on presently.

**Structure of the absorption spectrum**

From the mechanism described it might be inferred that resonance absorption occurs only at a single frequency, determined by (4a) or, if the frequency $f_0$ is given, at a certain induction $B_0$, given by:

$$B_0 = \frac{h}{2\mu_2} f_0.$$ 

The experiment shows, however, that absorption occurs in a certain region of $B$ values around $B_0$, and that the recorded absorption line thus has a certain width, and sometimes a certain structure. This may partly be attributed to the fact that, whereas a field $B$ has been applied and measured, the nuclei investigated may in reality be in a field that differs from $B$ by a small amount $b$. The resonance condition is then:

$$B + b = \frac{h}{2\mu_2} f_0 = B_0,$$

or

$$B = B_0 - b.$$ 

Absorption thus occurs at a value $B$ of the measuring field that differs from $B_0$. If $b$ differs for various parts of the specimen or for various kinds of nucleus, the result is a broadened line or a line spectrum. One may also conceive of performing the experiment such that the external field ($B_0$) is kept constant and the frequency $f$ varied. In that case resonance would occur when $f = f_0 + \Delta f = (2\mu_2/h)(B_0 + b)$, so that $\Delta f = (2\mu_2/h)b$. The value $\Delta f = 1$ c/s corresponds to $b = 2 \times 10^{-8}$ Wb/m$^2$.

Various reasons can be given for the occurrence of the field-strength deviations $b$. The first is quite trivial, being of an instrumental nature and connected with the fact that the magnetic field is not perfectly uniform. As a result, parts of the specimen are found in a field that is not exactly identical with the field $B$. This source of broadening can be reduced to negligible proportions by using small specimens and a magnet whose air gap is narrow compared with the diameter of the pole pieces. This applies at least to solids in which, for other reasons (to be discussed), marked broadening effects occur in any case. In liquids, which generally exhibit a spectrum having sharp resonance lines, the instrumental broadening may not be negligible.

Another cause of instrumental broadening is found especially when recording the spectra of solids. As we shall see, in such cases the measurement is performed by finding an average value over a range $\delta B$ of field strengths. Since $\delta B$ cannot be
made infinitely small, this also gives rise to line broadening (see later, fig. 10a).

The other causes of line broadening and of the occurrence of line spectra, discussed in the following, are essentially concerned with the physical conditions to which the nuclei are subject during the experiment, and about which the absorption spectrum can therefore provide information.

Local fields in crystals

For the present we shall confine the discussion to solids, that is to crystals. In a crystal the field acting on the nuclei consists of the external field $B$ (now assumed to be uniform) together with the dipole fields of neighbouring nuclei. For hydrogen nuclei this dipole field at a distance of $1\,\text{Å}$ is of the order of $10^{-3}\,\text{Wb/m}^2$. The total field acting on a nucleus subjected to a dipole field $b$ is $B + b$. At resonance we again have $B + b = B_0$, hence:

$$B = B_0 - b.$$  

The resonance line is then (in terms of $B$) displaced over a distance $b$.

A case frequently encountered is that of two neighbouring protons. This is found when investigating the absorption of two protons of a molecule of water of crystallization (H-O-H). The field $b$ caused by the one proton at the position of the other depends on the distance $r$ between the two protons and on the angle $\vartheta$ which the line connecting them makes with the external field $B$. The dipole field is given by:

$$b = \pm \frac{\mu_z}{r^3} (3 \cos^2 \vartheta - 1). \ldots \ldots \ldots \ldots$$

The $\pm$ sign arises because the "perturbing" proton can be oriented in two ways in the field $B$. For one pair of protons we then obtain, instead of a single resonance peak, two peaks at a distance $2b$ apart. We shall see presently that, as regards the magnitude of the effect, this statement requires some modification.

This, then, is the situation when we have a single crystal and consider the proton pairs therein which take up a specific orientation with respect to the crystal axes. If we turn from a single crystal to a powder, we find that the angle $\vartheta$ for the kind of proton pairs considered has a different value in each crystallite of the powder. The resonance pattern is consequently smeared out to a broad band in which, however, two peaks can still be recognized.

So far our discussion has taken account only of neighbouring protons forming a particular H-H pair, for example the protons of a single H-O-H molecule. These protons will also, however, be subjected to the dipole fields of protons of other H-O-H molecules and in addition to the dipole fields of other crystal nuclei. This causes a further broadening of the absorption pattern. As an example, fig. 2 shows the proton-resonance absorption of a powdered specimen of potassium fluoride (KF.2H₂O).

![Fig. 2. Spectrum of the absorption caused by proton resonance in a powder sample of potassium fluoride (KF.2H₂O).](image)

The dashed line represents the theoretical shape of the spectrum if there were only interaction between the protons of a single molecule of water. For calculating this curve the distance between the peaks was taken as $11 \times 10^{-4}\,\text{Wb/m}^2$, and the area below the curve was made equal to that under the experimental curve.

In the simple case of isolated proton pairs it is a fairly simple matter to predict a theoretical absorption curve that compares reasonably with the experimental result. In more complicated cases this is not so easy. In such cases, only the "second moment" of the broadened line is determined. If the line shape is given by

$$y = f(B),$$

its second moment is given by

$$\langle AB \rangle^2 = \int (B - B_0)^2 y\,dB \int y\,dB.$$

If the value of $\langle AB \rangle^2$ has been found experimentally, it can be compared with the theoretical value, for which Van Vleck derived the following 5):

$$\langle AB \rangle^2 = C \sum_{k} \sum_{j \neq k} (3 \cos^2 \vartheta_{jk} - 1)^2 r_{jk}^{-6}.$$

Here $r_{jk}$ represents the distance of a perturbing proton $(j)$ to the perturbed proton $(k)$, $\vartheta_{jk}$ the angle which the vector $r$ makes with the external field, and $C$ a constant comprising, among other things, the magnetic moments of the nuclei. The summation should really be extended over all the protons of the

crystal, but in practice it is sufficient to take only a small volume element of about 10 Å diameter.

Let us now return for a moment to the magnitude of the broadening. Apart from the "static" mutual interaction of the ions, referred to above, there is also a dynamic interaction, resulting from the fact that the protons, owing to their precession about the direction of the field, generate local alternating fields as well as a local static field. It would be going too far to deal with the complete quantum-mechanical treatment of this problem, which takes into account both the static and the dynamic effects \(^4\). The result, however, is fairly simple, and states that the expression \(3 \cos^2 \theta - 1\) occurring in the formula must be multiplied by a factor of \(\frac{1}{2}\), making the total broadening \(\frac{1}{2}\) times the static broadening.

If we consider only two protons, we see that they can orient themselves in three ways with respect to the field: both parallel, one parallel and the other anti-parallel, and both anti-parallel. This gives rise to three energy levels each being \(\Delta E = 2\mu_z B\) apart (see formula 2).

The mutual interaction described above (analogous to two coupled pendulums) perturbs the energy levels. As a result, the separation of the energy levels is now:

\[
\Delta E = 2\mu_z B_0 \pm 3\mu_z^2 r^2 (3 \cos^2 \theta - 1).
\]

This means that resonance is found for

\[
B = B_0 \pm \frac{1}{2} \mu r^2 (3 \cos^2 \theta - 1), \quad \ldots \ldots \ldots (6)
\]

which, except for the factor \(\frac{1}{2}\), is the same as (5). The factor \(\frac{1}{2}\) does not occur in the broadening caused by the influence of other nuclei on the protons, for which the static calculation gives the correct result.

**Interaction with the crystal lattice**

Apart from the interaction between the protons mutually and between the protons and other nuclei, interactions occur between the protons and the atoms of the specimen as a whole. This too gives rise to additional line broadening.

This additional broadening can be explained with the aid of Heisenberg's uncertainty principle. This tells us that the energy \(\Delta E\) of an excited state is indeterminate by an amount \(\delta E\), given by:

\[
\delta E \delta t \approx h. \quad \ldots \ldots \ldots \ldots (7)
\]

The quantity \(\delta t\) in the present case is a "relaxation time" \(\tau\), the significance of which is as follows. In the absence of an external field the spin directions are randomly distributed owing to thermal equilibrium. If, at a given moment, all spins were made parallel, then as a result of interaction with the lattice this ordering would relax and ultimately vanish according to an exponential law:

\[
e^{-\frac{\Delta E}{kT}}.
\]

In the case of protons in a liquid \(\tau\) is of the order of 10 sec and therefore \(\tau^{-1} = 0.1 \, \text{c/s}\). With the aid of (7) we find that this corresponds to an additional broadening of approximately \(2 \times 10^{-6} \, \text{Wb/m}^2\). In solids \(\tau\) may have a wide range of values, but the additional broadening here is, almost invariably negligible compared with the other causes of line broadening.

Thus, although the interaction with the lattice or with the environment is often negligible as regards the effect on the line width, it is really essential to the occurrence of resonance absorption. In an external field \(B\) in which there are \(N\) protons, the number of parallel-aligned protons \(N_p\), state 1) at thermal equilibrium is greater than the number of anti-parallel-aligned protons \(N_a\), state 2), to an extent given by:

\[
\frac{N_a}{N_p} = \exp (- \Delta E/kT), \quad \ldots \ldots \ldots (8)
\]

where \(T\) is the temperature and \(k\) is Boltzmann's constant \((k = 1.38 \times 10^{-23} \, \text{J/°K})\). If, now, an alternating field of the desired frequency is applied, and if there were no interaction with the lattice, after some time a state would arise where \(N_a = N_p = \frac{1}{2} N\). From that moment onwards as many protons would go over per unit time from state 1 to state 2 as from state 2 to state 1, and no absorption would be observed. The interaction with the lattice, however, tries to restore the situation (8); consequently, even when an alternating field is present, \(N_a\) remains greater than \(N_p\), and absorption can, therefore, still be observed. Also, it follows from this that, for the purpose of detecting the absorption, the alternating field should not be too strong. These points were already discussed in connection with paramagnetic resonance in the article quoted under 1).

**Structure of the spectrum in liquids**

In contrast to crystals, where the line widths may cover \(10^{-4}\) to \(10^{-2} \, \text{Wb/m}^2\), the resonance lines found for liquids are very narrow, of the order of, e.g., \(10^{-7} \, \text{Wb/m}^2\). Special measures, to be discussed later, are therefore necessary to keep the instrumental width (non-uniform field) below this limit. The fact that the marked line broadening found in crystals does not occur in liquids is due to Brownian motion which, in classical terms, so frequently perturbs the phase of the precessional movement that only the effect of the average field remains, the action of

neighbouring fields being eliminated by averaging with respect to time. The interaction with the medium remains as the sole cause of line broadening. As in crystals, however, this is a very slight effect.

The result of this situation is that, at field strengths of, say, $10^{-5}$ Wb/m$^2$, displacements and splittings of a resonance line are observed which are due to effects that may also be present in the solid but escape observation because of the large total broadening in the case of solids. These effects are largely attributable to the action of the magnetic fields of electrons. It is due to them that the spectra of various organic compounds differ so markedly from one another and can even be used for identifying these compounds. We shall deal with this subject at greater length when discussing the practical examples.

**Equipment for nuclear-magnetic-resonance investigations**

**Investigations on liquids**

As remarked, for observing nuclear magnetic absorption in liquids the magnetic field should be highly uniform. The field variation over the dimensions of the specimen (a few millimetres) should be less than $1 \times 10^{-6}$.

To obtain a sufficiently uniform magnetic field for these kinds of experiment, magnets are used, as mentioned above, in which the air gap is narrow compared to the diameter of the poles of the magnet. The pole pieces should be made of highly homogeneous material and ground optically flat. The remaining non-uniformity of the field is corrected by passing a current through suitably-positioned flat coils on the pole faces.

With the object of achieving a still higher resolution, the specimen is often rapidly rotated. This has a narrowing effect similar to that discussed above as regards the influence of the Brownian motion on the internal fields: the differences in macroscopic field strength are eliminated by averaging with respect to time. In this way a resolution of $10^{-8}$ Wb/m$^2$ can be achieved.

During the measurement the magnetic field should remain constant. In the case of an electromagnet, a highly stabilized current should be used, constant to within $10^{-6}$ of the desired value. Residual, relatively small fluctuations due to other sources are compensated by means of a coil of many turns wound round the magnet poles. The e.m.f. induced in this coil by a fluctuating magnetic field is amplified and converted into a current which is fed in anti-phase to a correction coil on the magnet. In this way a constancy of $3 \times 10^8$ can be maintained for several minutes.

An easier method to attain constant magnetic fields is to use a permanent magnet. The only important cause of deviations of the magnetic field in this case is that the magnetization of the magnetic material (e.g. "Ticonal") is temperature-dependent. The temperature of the magnet should change by no more than $10^{-4}$ °C if a constancy of $1 \times 10^8$ is to be attained. The magnet is therefore placed in a thermostat. Owing to the high thermal capacity of the magnet, a simple thermostat is sufficient to cope with the fluctuations of the ambient temperature.

The frequency of the applied alternating field, too, should have a stability of $1 \times 10^8$. This can be obtained by using a crystal-controlled oscillator placed in a thermostat. If a number of such crystals are available, various kinds of nuclei can be investigated. Since, however, as mentioned, nuclear magnetic resonance is mainly used for the investigation of organic compounds, the resonance of protons is of primary interest.

The variation of the magnetic field required for scanning the spectrum is produced by means of an additional excitation coil, through which a current is passed that rises very slowly and linearly from zero to a maximum (sawtooth waveform). In the case of a liquid spectrometer the maximum value of the field variation need only be quite small (a few $10^{-4}$ Wb/m$^2$).

Various types of high-resolution spectrometers are described in the literature, and some are also commercially available. As an example we shall mention some particulars of the high-resolution spectrometer marketed by Mullard (type SL 44 Mo2). This uses a permanent magnet which is accurately maintained at a constant temperature. The magnet gives a field of 0.9 Wb/m$^2$ and has poles of 15 cm diameter and a gap 3 cm in length. The resonance detector consists of a double-T measuring bridge, which is connected to a high-frequency amplifier, followed by a diode detector. The output voltage of this detector, which is proportional to the output voltage of the bridge, is applied to an oscilloscope having a long-persistence screen and to a recording unit. The bridge is fed by a crystal-controlled oscillator of 40 Mc/s. The specimen holder consists of a glass tube of 3 mm diameter, which is filled with the substance for investigation and rapidly rotated. The photograph in fig. 3 gives an impression of the equipment. A block diagram appears in fig. 4; some additional details are given in the caption.
Fig. 3. Mullard equipment for nuclear-magnetic-resonance investigations on liquids (high-resolution spectrometer, type SL 4·4·M02).

Investigations on solids

Since the width of the lines in solids is generally very large ($10^{-4}$ to $10^{-2}$ Wb/m$^2$), a highly uniform field is not necessary for absorption measurements on solids, nor need the field be so highly constant with time or the measuring frequency so stable.

On the other hand the absorption at a given field strength is now roughly a hundred times weaker. Compared with liquids, therefore, larger specimens are used and more sensitive equipment. The higher sensitivity is achieved by a different measuring procedure (see below). Higher demands are also made on the versatility of the spectrometer, since in solid-state investigations it may be necessary to measure the resonance of a large number of elements that may occur in crystals. Whilst the study of protons is often important for the determination of crystal structures (water of crystallization), the resonance of other nuclei (Cu, Al, etc.) enters into the study of metals. Investigation of the structure of the resonance line as a function of temperature, for example, makes possible the study of a number of effects (such as atom movements, which make the resonance line narrower, and diffusion phenomena).

As an example of a solid-state spectrometer we shall discuss the equipment used in the Philips Research Laboratories at Eindhoven. A block diagram of the set-up is shown in fig. 5.

Fig. 4. Block diagram of the Mullard spectrometer in fig. 3 used for liquid analysis. \( \text{Mgn} \) permanent magnet (induction in air gap 0.9 Wb/m$^2$). \( L \) alternating-field coil in which the sample is placed. \( O \) crystal oscillator, frequency 40 Me/s, for generating the high-frequency alternating magnetic field inside the coil \( L \). \( B \) measuring bridge. \( A \) preamplifier. \( R \) receiver. \( G \) diode detector. \( K \) cathode-ray oscilloscope. \( \text{Reg} \) recorder. \( \text{Var} \) generator of auxiliary current for the sawtooth variation of the static magnetic field used for scanning the spectrum. The current source \( \text{Sh} \) is used for correcting the magnetic field in the air gap to match it to the oscillating frequency of the crystal.
The field for this spectrometer is again generated by a permanent magnet. The fairly considerable range of field strengths required for the analysis of solids is obtained here by means of gaps of variable length in the yoke. With the aid of a cam the yoke bars can be raised, thereby decreasing the magnetic field. A particular advantage of this construction is that, within a certain range, the field can be reproducibly adjusted to any desired value, so that no auxiliary field is needed for matching to the oscillator frequency (cf. Sh in fig. 4).

The cam is driven by a synchronous motor via a gearbox, enabling the spectrum to be continuously scanned. The shape of the cams is such as to ensure the most linear possible variation of the field with time. As in the case of a high-resolution spectrometer, this is desirable in order that equal distances on the uniformly moving strip chart in the recorder will correspond to equal variations of $B$.

To the slow field variation a low-frequency sinusoidal modulation of very small amplitude is added (coils $L_{\text{mod}}$ and oscillator $O_{\text{mod}}$ in fig. 5). Fig. 6 shows what happens. A portion of the resonance line of width $\delta B$ is scanned. The resultant signal, when $\delta B$ is sufficiently small, is proportional to the derivative $dy/dB$ of the absorption curve $y = f(B)$.

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![Diagram](image-url)
This method of measurement has the advantage over the simpler method used for liquids that amplification is now possible in a very narrow band around the modulation frequency (230 c/s). As a result the unavoidable noise from the amplifier is suppressed and a considerable gain is achieved in the signal-to-noise ratio.

This method cannot be used with the liquid spectrometer because the line width, expressed in terms of frequency, is so very small (0.1 c/s). Modulation with a practical frequency, which must be at least thirty or forty c/s, would give rise to undesirable line broadening and satellite lines. However, since the absorption intensity in liquids is so much greater, a lower sensitivity is sufficient in their case.

The signal is detected, in the present equipment, with the aid of the same oscillator \(^7\) that supplies the high-frequency voltage to the alternating-field coil. This is done by making the coil form part of the frequency-determining network of the oscillator. A small change in the properties of the coil (the Q changes depending on the absorption of the specimen inside it) causes a considerable change in the voltage of the oscillator.

After detection the low-frequency signal is amplified in a narrow-band amplifier (A in fig. 5) and mixed with an alternating voltage whose frequency is equal to the modulation frequency. This finally produces a D.C. voltage which is proportional to the derivative of the resonance peak and is recorded on a strip chart. Examples of such recordings appear in fig. 10.

A second specimen and coil are present in the magnetic field. By means of proton resonance in this (liquid) specimen the magnetic field is continuously measured and calibrated by comparison with the signal from a crystal-controlled oscillator (J in fig. 5). The calibration marks appear on the recording. In the present equipment the distance between the marks is 1.17 x 10^{-4} Wb/m\(^2\). This again clearly demonstrates the difference between the spectra of liquids and solids. Broadly speaking, about 20 calibration marks appear on one spectral line in the case of solids, whereas there may be 20 complete liquid spectra between two such calibration marks.

For measurements at low temperatures the complete specimen holder can be placed in a cryostat. With the set-up now in use, measurements can be made at temperatures as low as 20 °K; the recent availability of liquid He now makes it possible to measure down to 1.2 °K.

The caption to fig. 5 gives further particulars of the equipment. The photograph in fig. 7 gives an impression of the set-up. The permanent magnet is shown separately in fig. 8, showing the mechanism for varying the air gap.

In the adjoining table some properties of the two nuclear magnetic spectrometers discussed are set out side by side.

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<td>1 : 2 x 10(^9)</td>
<td>1 : 5 x 10(^4)</td>
</tr>
<tr>
<td>Suitable for the nuclei: especially (^1H)</td>
<td>numerous</td>
<td></td>
</tr>
<tr>
<td>Modulation of static magnetic field</td>
<td>sawtooth</td>
<td>sawtooth + low-freq. sine wave</td>
</tr>
<tr>
<td>Amplitude of sawtooth</td>
<td>0.0002 Wb/m(^2)</td>
<td>0.03 Wb/m(^2)</td>
</tr>
<tr>
<td>Recorded quantities</td>
<td>absorption (y = f(B))</td>
<td></td>
</tr>
<tr>
<td>Measurement at low temperatures</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

There now follow some simple examples of the practical application of nuclear magnetic resonance.

**Examples**

**The spectrum of ethyl alcohol**

The ethyl-alcohol spectrum reproduced in fig. 9 was recorded with a Mullard spectrometer. The spectrum consists of a number of very fine lines, and its total width is only 5 x 10^{-6} Wb/m\(^2\). Since it is the spectrum of a liquid, the marked broadening usually found in solid spectra is lacking. The lines are due to hydrogen nuclei in the sample.

Let us now examine the structure of the spectrum more closely. There are three groups of lines. The integrated areas of each of the three groups are found to be in the ratio 3 : 2 : 1, corresponding to the formula \(\text{CH}_3\text{CH}_2\text{-OH}\). Why have these three groups a slightly different frequency and why is each group split into components (viz. 3, 4 and 1)?

The magnetic field at the position of one of the protons of the molecule is composed of the externally applied field plus the field produced by the surround-

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ing valency electrons. The electron density in the molecule is lowest in the OH group and highest in the CH₃ group, and for this reason the electron field differs for the three groups that make up the molecule. This causes the splitting into three groups of lines.

The splitting into components of a single group of lines arises as follows. The electrons move through the entire molecule and, as it were, communicate information to the nuclei regarding their immediate environment. Since, for example, the protons of the CH₂ group can assume different orientations in relation to the external field, the electron orbits can be polarized in different ways by the spin field of these protons. This gives rise to a change, albeit a very small one, in the magnetic field which the electrons produce at the position of the neighbouring groups. The two protons of the CH₂ group may either be both parallel with the measuring field, or one may be parallel and the other anti-parallel, or both anti-parallel. The total magnetic moment of
the CH₂ group is then respectively $2\mu_z$, zero or $-2\mu_z$. The probabilities of these three cases occurring are in the ratio of 1 : 2 : 1. This causes the line belonging to the protons of the CH₃ group to be split into three components with an intensity ratio of 1 : 2 : 1. In the same way we can argue that the line pertaining to the protons of the CH₂ group is split, under the influence of the neighbouring CH₃, into four components with an intensity ratio of 1 : 3 : 3 : 1.

Special considerations apply to the line due to the OH group. One might expect that this line, under the influence of the neighbouring CH₂ group, would also be split into three components of intensity ratio 1 : 2 : 1. Only one line, however, is in fact found. The explanation is that the alcohol sample used contains impurities in the form of traces of water, acid or base. Since the electron density around the OH group is small, the proton of the OH group can easily break away. Where traces of impurity are present there is therefore a constant exchange between the H ion of the OH group and the H ions of the impurity. This proton exchange occurs for every molecule very many times per second. The time during which a proton of the OH group is under the influence of the polarized electron orbits in the alcohol molecule is therefore extremely short, and the average frequency of the exchange is high compared with the frequency difference between the splitting components of the line group, which would exist if there were no such exchange (approx. 10 c/s). As a result there is no effective splitting into components. In extremely pure alcohol the line of the OH group does show the expected splitting into three components.

The further details visible in the spectrum are due to second-order effects which do not enter into the scope of this simple explanation and will not be discussed.

It should be noted that the described spin-spin interaction, via the polarization of the electron orbits, differs essentially from the direct spin-spin interaction which occurs in solids and which, in our case, is made ineffective by the Brownian motion of the molecules.

The above inferences drawn from the nuclear magnetic resonance spectrum are an elegant confirmation of the structure of the alcohol molecule, already determined by other means. It is evident that in other cases valuable information can be obtained from liquid spectra, that can serve for determining an unknown structure.

The other examples to be discussed refer to solids. They concern investigations made, or still in progress, in Philips Research Laboratories at Eindhoven, and in all cases involve proton resonance.

**Hardening of “Araldite”**

The hardening of “Araldite” (Ciba, Basle) is a striking example of the transition of a fluid into the solid state. Araldite is a widely used synthetic adhesive of the epoxy-resin type. The adhesive consists of two fluid components, the epoxy resin and a hardening agent added and mixed just before use. After about 30 hours the adhesive has set hard as a result of polymerization of the epoxy molecules. Some spectra, recorded at various times during the hardening process, are shown in figs. 10a, b and c. It can be seen how the original very narrow liquid
line, whose width is determined by instrumental causes, develops into a solid-state line having a width of about $2 \times 10^{-3} \, \text{Wb/m}^2$. The variation of the second moment with time indicates that the line broadening takes place in several more or less distinct stages. This allows inferences to be drawn regarding the gradual slowing-down of the motions of various groups of atoms in the molecule. This subject has been studied more extensively by Lösche $^8$.

**Motion of hydrogen gas in metals** $^9$

The following example refers to the motion of hydrogen gas in metals. Some metals and alloys can absorb relatively large amounts of gas, e.g. hydrogen, and for this reason they can be used as getters in radio valves. One of these alloys is thorium-aluminium, Th$_2$Al. The crystal structure of this alloy has been extensively studied $^{10}$, and it is found that a maximum of four atoms of hydrogen is taken up per molecule of Th$_2$Al. Between the metal atoms are two interstices, each of which can entrap two H atoms. We shall consider the compound Th$_2$AlH$_2$, in which half the number of available interstices are filled.

At room temperature a very narrow resonance line was found with this compound. Partly from the intensity distribution in the line it was concluded that this narrow line is due to protons that jump very rapidly from one interstice to a neighbouring unoccupied one. Owing to this movement the dipole-dipole interaction between neighbouring protons is averaged out. At low temperatures ($T < 100 \, ^\circ\text{K}$) a line width of $8 \times 10^{-4} \, \text{Wb/m}^2$ was found. Since $8 \times 10^{-4} \, \text{Wb/m}^2$ corresponds to a frequency difference of about $4 \times 10^4 \, \text{c/s}$, it may be inferred from this that under these circumstances the time spent by a proton in an interstice is long in relation to $3 \times 10^{-5} \, \text{sec}$. Measurement of the line width as a function of $T$ produced the curve shown in fig. 11.

From the temperature at which the line-narrowing begins, in conjunction with the value of the line width at low temperature, it is easy to determine the way in which the average jump frequency $v_s$

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depends on the temperature. With a minor simplification this can be described by the formula:

\[ \nu_s \propto \exp \left( -\frac{E_a}{kT} \right), \]

where \( E_a \) represents the activation energy of the diffusion process. This is found to be equal to 0.22 eV. From the intensity distribution of the absorption line it can be inferred that at low temperature short-range ordering of the protons exists. This investigation is being pursued.

Fig. 11. Line width of the resonance in Th₄AlH₄ as a function of temperature.

Positions of protons in aluminium hydroxides

To illustrate the application of the second-moment determination discussed above, we shall consider an investigation of aluminium hydroxide. Various hydroxides of Al are known, each with its own crystal structure; examples are hydrargillite (\( \gamma \)-Al(OH)₃), bayerite (\( \alpha \)-Al(OH)₃) and boehmite (\( \gamma \)-AlOOH). We shall deal here with the first compound mentioned. The O atoms in this compound form a triangular layer structure. There are several conceivable sites for the H atoms; two are represented in fig. 12a and b. The theoretical value of the second moment (with an O-H distance of 0.96 Å) is \( 26 \times 10^{-8} \) (Wb/m²)² in the case a, and \( 29.4 \times 10^{-8} \) (Wb/m²)² in the case b. The value found by experiment is \( (26.5 \pm 1.2) \times 10^{-8} \) (Wb/m²)², which argues in favour of the first assumption. Other crystal models that have been proposed give a widely different value, e.g. \( 15 \times 10^{-8} \) (Wb/m²)², and must therefore be rejected.

Finally, it may be noted that the few, very simplified examples of applications discussed here are by no means representative of all the possibilities offered by nuclear magnetic resonance. A list of the publications that have appeared so far on the subject of nuclear magnetic resonance would take up just as many pages as this article.

Appendix: Comparison of nuclear magnetic resonance and paramagnetic resonance

In the introduction to this article mention was made of the relation between the phenomena of nuclear magnetic resonance and paramagnetic resonance. It is perhaps useful to touch here on some of the essential points of difference, some of which have already appeared in the foregoing pages.

The measurement techniques used for studying the two effects differ primarily in the wavelengths employed: paramagnetic-resonance investigations are performed at centimetric wavelengths, and thus use klystrons, waveguides and so on. Nuclear magnetic resonance is studied at wavelengths of some tens of metres, which calls for ordinary radio valves and transmission lines. This frequency difference is directly connected with the fact that the magnetic moment of the electron, which is equal to \( \hbar/4\pi m \) (Bohr magneton), is roughly 1000 times greater than that of the proton or other nuclei. Nuclear moments according to equation (1) are principally given by \( \hbar/4\pi m \) (nuclear magneton). As a result the two possible states for an electron (with a spin parallel or anti-

\[ \hbar/4\pi m \]
parallel to the external magnetic field) show an energy difference $\Delta E$ roughly 1000 times greater than that for a proton (see eq. (2)). Accordingly the frequency $f_k$ at which nuclear magnetic resonance occurs (see eq. (4)) is given by:

$$f_k = \frac{g}{4 \pi m_P} B,$$

and the frequency of paramagnetic resonance $f_e$ (see eq. (5) in article 1) is given by:

$$f_e = \frac{g_e}{4 \pi m} B.$$

Since, for practical reasons, the magnetic fields $B$ for observing the absorption due to electron spins and due to nuclear spins are chosen at the same order of magnitude (0.1 to 1 Wb/m²), and since the numerical factors $g$ and $g_e$ in both formulae do not differ appreciably ($g_e \approx 2$, and $g$ lies between 0.1 and 10, as mentioned earlier), we see that the resonance frequencies in the two methods differ by a factor of the order of 1000 (proton mass $m_P = 1836$ times electron mass $m$).

Another practical and very important difference between the two methods discussed concerns the sensitivity. The measurement of paramagnetic resonance is very much more sensitive than the measurement of nuclear magnetic resonance. This is again a direct consequence of the fact that for an electron the two possible states with opposite spin orientations show an energy difference $\Delta E$ about 1000 times greater than for a proton (confining ourselves now to protons). The relationship can be understood as follows. The difference between the numbers of protons and electrons in the two states mentioned is proportional to $\Delta E$ (see eq. (6), which is also valid for electrons). The number of electron spins that can contribute to energy absorption from the alternating field is therefore about 1000 times greater than the number of proton spins, the total number per unit volume being the same. Moreover the energy quantum $\Delta E$ absorbed from the alternating field upon each transition between the two states is also about 1000 times greater (this has already appeared in the frequency difference), so that the energy absorption — or the measured signal — other conditions being the same, is about $10^9$ times greater for electrons than for protons.

True, the detectors used for centimetric waves give a much poorer signal-to-noise ratio than those for wavelengths of some tens of metres, and also the line width (to which the recorded intensity is inversely proportional) is several times larger in parametric resonance than in nuclear magnetic resonance. Nevertheless the first method referred to remains far more sensitive than the other, which means that paramagnetic-resonance investigations can be applied for very much smaller concentrations of resonators.

It is precisely for this reason that such useful results have been achieved with paramagnetic resonance: the paramagnetic centres are usually present in only low concentrations, whereas in nuclear-magnetic-resonance studies the whole of the investigated substance enters into the measurement.

This brings us to the last point of difference to be noted, which concerns the information obtainable with the two methods. Paramagnetic resonance provides information about the immediate environment of a paramagnetic centre. Nuclear magnetic resonance, on the other hand, gives information on the structure of molecules or of crystals as a whole, and on the effects of impurities (also non-paramagnetic impurities) on that structure.

A recent further development of the techniques discussed is the study of double resonance, where paramagnetic and nuclear magnetic resonance are excited in a substance simultaneously. This allows the nuclear magnetic resonance signal to be intensified, so that nuclei present in small concentrations are also accessible to investigation 12). Moreover, the paramagnetic-resonance spectrum is influenced by the transitions between the energy levels of different nuclear spin orientations 12). As a result still more particulars can be learned about the properties of the solid state. There is no space here, however, to deal at greater length with these methods and their application.


13) This method is also referred to as "Endor" (electron nuclear double resonance). See e.g. G. Feher, Electron spin resonance experiments on donors in silicon, Phys. Rev. 114, 1219-1244, 1959 (No. 5).

Summary. Nuclear magnetic resonance gives rise to the specific absorption of electromagnetic waves (best measurable at metre wavelengths) by certain atomic nuclei, particularly hydrogen nuclei, when these are placed in a constant magnetic field. Since the resonance of a given nucleus is affected by the fields of neighbouring nuclei and electrons, the nuclear magnetic absorption spectrum offers a variety of information on the substance containing the nuclei. In solids the effect appears in a marked broadening of the resonance line; in liquids it appears in a splitting of the line into several components grouped closely together. A concise explanation of the theory of the phenomenon is followed by a description of two equipments used for recording the absorption spectra, one for liquids and the other for solids. The essentially different requirements of these two cases are dealt with at some length. In conclusion some examples are discussed of the numerous uses to which nuclear magnetic resonance has already been put, which include the identification of compounds (analysis of organic liquids) and the structural analysis of molecules and crystals.