Nuclear Magnetism in Relation to Problems of the Liquid and Solid States

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THE MAGNETIC BEHAVIOR OF MATTER in the bulk—paramagnetism, diamagnetism, and ferromagnetism—can be traced to the electronic structure of the atoms of which the matter is composed. The *electron,* in short, is the cause of ordinary magnetism. But the electron is not the only magnetic constituent of most substances, for many atomic *nuclei* have certain magnetic properties. Although the magnetic effects to which these nuclear properties give rise are too feeble to be observed under most circumstances, it has been possible to devise techniques which bring them into prominence. From these experiments in nuclear magnetism one learns more about the nucleus, and, since the most active frontier in physics lies at the nucleus, such information is highly prized. In quite another direction, however, a line of approach is opened to certain features of the structure of liquids and solids which prove to be involved in an interesting and unusual way in the manifestations of nuclear magnetism.

It is the latter aspect of nuclear magnetism that I propose to survey in this article, after providing an introduction to the magnetic properties of nuclei and to the phenomenon of resonance upon which the experimental method depends. "Survey" is perhaps too ambitious a term, for any attempt to predict the ultimate extent or importance of this new field must be renounced at the outset.

Nuclear Spins and Magnetic Moments

In addition to their more familiar properties of mass and electric charge, many atomic nuclei possess intrinsic angular momentum, or "spin," and magnetic moment; that is to say, the nucleus behaves like a spinning top with a magnet embedded along its axis. It is natural to seek the origin of nuclear magnetism in the motion of the positive electric charge of the nucleus; charge in motion is the same as electric current, and electric currents produce magnetic fields. We are thus led to regard the proton, for example, as a positively charged sphere spinning with a certain angular momentum and equivalent, in its magnetic properties, to an infinitesimal magnetic dipole. Although such a view eventually proves inadequate, it will serve very well as a basis for our discussion.

The intrinsic angular momentum of a nucleus is specified, in units of $h/2\pi$ (h = Planck's constant), by the number I, which is either integral or half-integral. The quantity $Ih/2\pi$, to be more explicit, is the maximum component of the angular momentum vector measured along a selected direction. The magnetic moment, μ (the strength of the nuclear dipole), is conveniently expressed as a multiple of a unit called the *nuclear magneton* and defined as $eh/4\pi Mc$, where e is the electronic charge; M, the mass of the proton; and c, the speed of light. Nuclear magnetic moments are, in general, of the order of magnitude of one nuclear magneton. The intrinsic magnetic moment of the *electron,* by contrast, is $eh/4\pi mc$, where m is the electronic mass. Thus, nuclear magnetic moments are roughly 1,000 times smaller than electronic moments.

The spin number, I, of a given nuclear species and, so far as we know, the magnetic moment, μ, are permanent, sharply defined characteristics of the nucleus, not to be altered by any means short of raising the nucleus to an excited state, a comparatively violent process with which we shall not be concerned.

The properties of spin and magnetic moment were first attributed to nuclei in 1924, by Pauli, to account for the so-called *hyperfine* structure of lines in the spectra of certain elements. Such a line, analyzed with a spectrograph of high resolving power, had been found to consist of a very closely spaced group of lines, or multiplet—an effect which could be explained by taking account of the interaction of the nuclear magnet with the magnetic fields arising from the motion of the electrons in the atom. The recognition by Goudsmit and Uhlenbeck of the intrinsic spin and magnetic moment of the electron itself, and the subsequent rapid progress in the correlation of atomic spectra with atomic structure, opened the way to a complete quantitative interpretation of hyperfine structure. The magnitude of the nuclear angular momentum and magnetic moment could, in turn, be deduced from the results of hyperfine structure measurements.

To determine the nuclear magnetic moment by this means one must measure the separation in frequency of exceedingly closely spaced spectral components. Very precise values can seldom be obtained, despite the remarkable advances in high-resolution spectroscopy which this challenging problem has called forth. The nucleus is an extremely feeble magnet, and this is the cause of the difficulty. The energy differences involved in the interaction of the nuclear magnet with the surrounding electrons, or with an applied magnetic field, are usually not larger than 10^{-20} to 10^{-18} ergs. According to the Bohr relation, $\Delta E = h\nu$, the corresponding frequencies lie in the band of ordinary radio frequencies or at most, in a few extreme cases, in the region of centimeter-wave lengths.

The possibility is thereby suggested of measuring such weak interactions directly, by detecting the absorption or emission of waves of radio frequency. Just this has been done in the celebrated molecular beam experiments of Rabi and his students at Columbia (*7*). By this form of radio-frequency spectroscopy,[1] augmented in some cases by the more recent—although in many respects more conventional—radio-frequency methods to be described presently, the magnetic moments of nearly 40 nuclear species have been determined with high precision. Hyperfine structure measurements in the optical region have established the spins and, at least approximately, the magnetic moments of about 35 additional species. There are left, among the stable nuclei which would be expected to possess magnetic moment, more than 40 which are still unmeasured.

The spins and magnetic moments of several nuclear species are listed in Table 1. Most of the entries in this abbreviated table originated in the Columbia molecular beam laboratory. The magnetic moment of the neutron deserves special mention. This was first measured by Alvarez and Bloch, at Berkeley, by an ingenious adaptation of molecular beam principles; the value listed was obtained more recently by Arnold and Roberts, at the Argonne Laboratory, by a refinement of the same method. The precision with which nuclear magnetic moments can now be compared is not fully displayed in the tabulations. For example, Bloch has recently redetermined, at Stanford, the ratio of the magnetic moment of the proton $_1H^1$ to that of the deuteron $_1H^2$, obtaining 3.257195 ± 0.00002. The magnetic moment of the triton $_1H^3$, a novel particle still unavailable in most laboratories, is equally well established.

TABLE 1

NUCLEAR SPINS IN UNITS OF $h/2\pi$, AND NUCLEAR MAGNETIC MOMENTS IN UNITS OF THE NUCLEAR MAGNETON, μ_0, OF THE NEUTRON, THE TRITON, AND THE STABLE NUCLEI THROUGH O^{16}*

Nucleus	I	μ/μ_0	Nucleus	I	μ/μ_0
$_0n^1$	1/2	−1.910	$_4Be^9$	3/2	−1.176
$_1H^1$	1/2	2.7896	$_5B^{10}$	1	0.598
$_1H^2$	1	0.8564	$_5B^{11}$	3/2	2.687
$_1H^3$	1/2	2.9756	$_6C^{12}$	0	0
$_2He^3$	1/2	?	$_6C^{13}$	1/2	0.701
$_2He^4$	0	0	$_7N^{14}$	1	0 403
$_3Li^6$	1	0.8214	$_7N^{15}$	1/2	0.280
$_3Li^7$	3/2	3.2535	$_8O^{16}$	0	0

* The sign of the magnetic moment refers to the polarity of the nuclear dipole with respect to the direction of the angular momentum vector.

The table discloses no obvious systematic variation of the magnetic moment, μ, with charge and mass number. So far as the spin is concerned, two general rules can be stated: (1) The spin number, I, is an odd or an even multiple of $\frac{1}{2}$ as the mass number, A, is odd or even; this is a direct consequence of the half-integral spins of the nuclear constituents, the neutron and the proton. (2) A nucleus that contains an even number of protons and an even number of neutrons, such as $_8O^{16}$, or $_{38}Sr^{88}$, has zero spin and moment; this is an empirical rule to which no exception has yet been discovered. Further than this, the task of relating quantitatively the magnetic moments of nuclei to the details of nuclear structure remains one of the larger problems of theoretical nuclear physics. A beginning has been made among the light nuclei (*2*), but beyond the limits of Table 1, roughly, even an approximate theory is lacking. The depth of the problem, as well as the inadequacy of the spinning, charged sphere as a model of the nucleus, is suggested by the fact that the neutron, an uncharged "elementary" particle, has a magnetic moment!

Fortunately, we need not concern ourselves here with the details of nuclear structure. In the experiments to be described, the nucleus can be regarded merely as a carrier of magnetic moment and angular momentum to which the rules of quantum mechanics apply. We shall be interested in the interaction of the magnetic nucleus with its surroundings and with an externally applied magnetic field. It will not seriously restrict the discussion if we confine our attention to a single nucleus, the proton, which has, according to Table 1, the intrinsic angular momentum $\frac{1}{2}(h/2\pi)$ and a magnetic moment amounting to 2.7896 nuclear magnetons.

RESONANCE ABSORPTION

The emission or absorption of light by a free atom takes place in accordance with the resonance condition which quantum theory permits us to express in the following way: The possible states of an isolated atom include a sequence of discrete states sharply defined with respect to energy; a transition of the system from one of these states to another, differing in energy from the first by ΔE, is accompanied by emission (or absorption) of light of the frequency $\nu = \Delta E/h$ (h = Planck's constant).

Consider, for the moment, a free proton in a magnetic field of strength H_0. Ignoring the translational

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[1] The rapidly growing field of radio-frequency and microwave spectroscopy, which has applications much broader than the scope of the present article, has been surveyed by Roberts in *Nucleonics,* October 1947.

degrees of freedom, which are here irrelevant, this simple system will be found in one of two possible states which differ in the orientation of the spin axis of the proton with respect to the magnetic field. That is, the component, in the direction of the magnetic field, of the angular momentum vector can assume either of the values $+h/4\pi$ and $-h/4\pi$. (For a particle of spin I there are $2I+1$ possible states, or spin orientations.) The two states differ in energy, for the component of nuclear magnetic moment in the direction of the field is $+\mu$ in one case and $-\mu$ in the other. In fact, the difference in energy is just $2\mu H_0$, the work that would be required to reverse the direction of a magnet of strength μ which had originally been aligned with a field H_0. The two states will be denoted by (+) and (−), the (−) referring to the state of higher energy in which the nuclear magnet is directed counter to the magnetic field. Actually, the spin axis of the nucleus lies in neither case parallel to the direction of field H_0, but is tipped at a considerable angle and precesses about the direction of the field, like the axis of a tilted top. This does not complicate matters, for it is only the components of spin and magnetic moment parallel to H_0 which concern us, and it is just these components which are specified by I and μ.

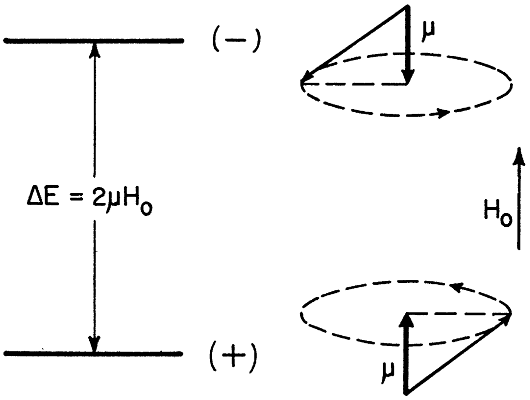

FIG. 1. The two energy states of a proton in a magnetic field, H_0. The energy levels are drawn at the left.

The situation is illustrated in Fig. 1, in which the energy level scheme appears. By exposing the system to radiation of the proper frequency, it should be possible to bring about a transition from one of the two states to the other, with the consequent absorption of a quantum of energy, in a (+) → (−) transition, or emission of a quantum, in a (−) → (+) transition. In the former case, *resonance absorption* will have occurred; the latter process is usually called stimulated emission, although, as it is the exact counterpart of the former process, it might well be called resonance emission. For a proton in a magnetic field, H_0, of 10,000 gauss, the resonance frequency, computed from $\nu = \Delta E/h = 2\mu H_0/h$ turns out to be about 41 megacycles/sec. The radiation required is therefore a radio wave, or, since only the magnetic field of the wave would be effective anyway, merely an oscillating magnetic field such as one might make by passing a radio-frequency current through a suitable coil.

Transitions of the sort described are the basis of the magnetic resonance method of molecular beams. The nuclei involved are located in electrically neutral molecules—a bare proton would be unmanageable for fairly obvious reasons. The problem is not seriously complicated by the presence of the surrounding constituents of the molecule. The molecule itself moves through a highly evacuated chamber and remains exceptionally *free* during its exposure to the radio-frequency oscillating field. It is therefore not surprising that sharply defined resonance effects can be observed. It will be recalled that one of the conditions essential for obtaining sharp lines in ordinary spectroscopy is that the emitting atoms occupy a region of relatively low pressure. The frequency of atomic collisions sets a limit on the lifetime of an excited state and hence (a familiar illustration of the uncertainty principle) limits the precision with which the energy of such a state can be specified, with a consequent broadening of the observed spectral line. This "collision broadening" becomes more pronounced as the pressure is increased until eventually the line structure of the spectrum is obliterated and we observe the continuous emission spectrum characteristic of an incandescent solid.

It might be expected that even lower pressures would be necessary for successful radio-frequency spectroscopy, which is concerned with extremely small energy differences. Low pressures are indeed necessary wherever atomic or molecular states are involved, a pressure as low as 10^{-5} atmospheres being required to reduce the width of a spectral line to 100 kilocycles/sec. The nucleus, however, occupies a uniquely isolated and protected position in the interior of the atom. More important, the states (+) and (−) in Fig. 1 can be perturbed only by *magnetic* fields, and in the majority of substances the electrons, which would otherwise cause strongly perturbing magnetic fields, are paired off in such a way that their net magnetic effect is zero. For this reason it has been possible to observe sharply defined resonance absorption, due to transitions of the type (+) → (−), in ordinary solids and liquids containing magnetic nuclei.

When such a substance—a drop of water, for example, or a lump of paraffin—is placed in a strong magnetic field, it can be regarded in first approximation as a mere collection of a large number of protons, for each of which the two energy states, (+) and (−), are available. With the application of a weak radio-frequency magnetic field, oscillating at precisely the frequency of resonance, protons which were in the (+) state will make transitions to the (−) state and *vice versa*. The *vice versa* is important; in fact, the "up" and "down" transitions are induced with *equal probability,* and if the protons were initially equally divided between the two states, no *net* absorption of energy can occur. If the resonance effect is to be detectable, an inequality of the population of the two levels must be established. This will come about if the magnetic nuclei can transfer energy to, and come into thermal equilibrium with, their surroundings, for in thermal equilibrium the lower of the two energy levels will be favored with the larger population. At any easily attainable temperature the excess in the lower state is very slight; the ratio of the number of nuclei in the upper state to the number in the lower state is the well-known Boltzmann factor, $e^{-h\nu/kT}$, which, for $\nu = 40$ Mc/sec and $T = 300°$ K, is 0.9999934. It is upon the fractionally minute surplus of nuclei in the lower state that the observed effects entirely depend.[2] We shall inquire later into the means by which thermal equilibrium is established, thereby discovering a rather surprising situation. At present we shall assume that it can be attained somehow, and turn to the detection and interpretation of nuclear resonance absorption.

The method of observation is extremely simple in principle. Approximately 0.5 cc of water (for example), contained in a glass tube, is surrounded by a coil consisting of a few turns of copper wire. The coil is connected into a radio-frequency bridge circuit which is excited by an oscillator at, say, 40 Mc/sec. The coil with its water "core" is located within the field of a strong magnet. When the resonance condition is attained by adjustment of the frequency or of the strength of the magnetic field (usually the latter is easier) the absorption of energy by the protons in the water is manifested as a change in the apparent resistance of the coil. Because the effect to be detected is extremely feeble, the apparatus is actually more elaborate than the above description might suggest. However, a full description of the experimental technique, which can be found elsewhere (*5*), is not necessary for the present discussion.

The method outlined is essentially that used in the first observation of nuclear magnetic resonance absorption at Harvard in 1946 (*10*). At the same time and independently, Bloch, Hansen, and Packard, at Stanford, demonstrated the closely related phenomenon which Bloch has named *nuclear induction* (*3, 4*). The two methods take advantage of somewhat different manifestations of the same fundamental process; there may be areas of investigation where one or the other is preferable, but both are coming into general use.

The resonance absorption by protons in water is displayed in Fig. 2, a reproduction of an oscilloscope trace obtained while sweeping through the resonance line by varying the magnetic field, H_0. The value of H_0 at resonance was 6,940 gauss in this experiment, the radio frequency being 29.5 Mc/sec. The total range covered in the picture is 2 gauss; thus, resonance absorption occurs within an interval of only 0.2 gauss. The equivalent line width on a frequency scale is about 1 kilocycle/sec, or roughly 10^5 times smaller than the width of a typical sharp line in the visible spectrum.

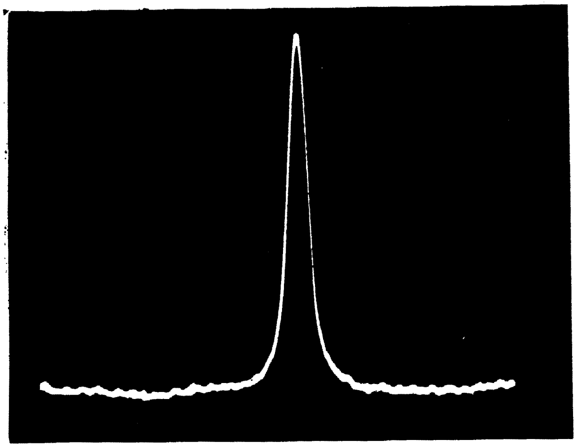

FIG. 2. Resonance absorption by protons in water, recorded on an oscilloscope.

In other substances containing protons an absorption line is observed at precisely the same value of the magnetic field, if the radio frequency is the same. This was to be expected, for the resonance condition involves only the specifically nuclear property, μ/I. However, the *width* of the line varies greatly from one substance to another. The proton resonance in ice, for example, is found to be 20–50 times as wide as, and correspondingly weaker than, the resonance shown in Fig. 2. In some crystals even more striking effects are observed. The proton resonance line develops a more complicated shape, or even breaks up into several more or less well-resolved components. A few typical examples are sketched in Fig. 3, beginning with the intense narrow line which is observed in water and in many other liquids. The peak intensity of the absorption is inversely related to the line width, other things being equal; the quantitative examination of the broad, and therefore weak, lines illustrated in Fig. 3 (b, c, d) calls for the utmost refinement in experimental technique.

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[2] Another consequence of the surplus in the lower state is that the sample is feebly magnetized; that is, it displays static paramagnetic susceptibility. In a remarkable experiment performed in Russia in 1937, Lasarev and Schubnikov succeeded in detecting the paramagnetism caused by the protons in solid hydrogen, at 2° K.

These effects are not to be explained in terms of nuclear properties alone, but are connected with the perturbing magnetic fields which originate in the immediate surroundings of a given hydrogen atom and which depend on, and are modified by, the *location* and *motion* of neighboring atoms. The investigation thus leads back into the physics of the liquid and solid states.

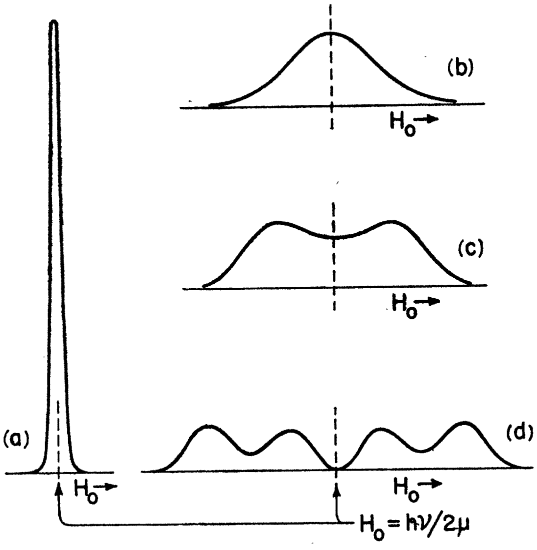

FIG. 3. The shape of the proton resonance absorption line in four substances: (a) water; (b) ice; (c) powdered gypsum, $CaSO_4 \cdot 2H_2O$; (d) a single crystal of gypsum, suitably oriented with respect to the magnetic field. The contrast between a typical liquid line (a) and the others is actually much greater than the sketch suggests; were the drawing to scale, (a) would be several times higher and narrower than shown above.

INTERPRETATION OF LINE WIDTH AND LINE STRUCTURE

The nuclei are, of course, not *entirely* isolated from magnetic disturbances of local origin. The most obvious sources of perturbing magnetic fields are the magnetic nuclei themselves. A selected proton in a drop of water is subject not only to any field which we may apply with an electromagnet, but also to the magnetic fields arising from the magnetic moments of neighboring protons in the liquid, including that of the other proton in the same water molecule. (The oxygen nucleus, as Table 1 indicates, is not magnetic.) The sum of all such perturbing fields, measured at the location of a given proton—but, of course, excluding the field of that proton—we shall call the "local field," H_{loc}. The local field will vary in magnitude and direction, from point to point in the material. It may also vary in time. The nature of these variations must now be discussed.

The magnetic field produced by a proton resembles that of a short bar magnet. The strength of the field decreases with the inverse cube of the distance. The "lines of force" surrounding such a magnetic dipole are indicated in Fig. 4. The dipole can represent the z-component of the magnetic moment of a proton in the state (−). Let us consider only the z-component of the *field* produced by the dipole, μ, at some nearby point P which might be the location of another proton.

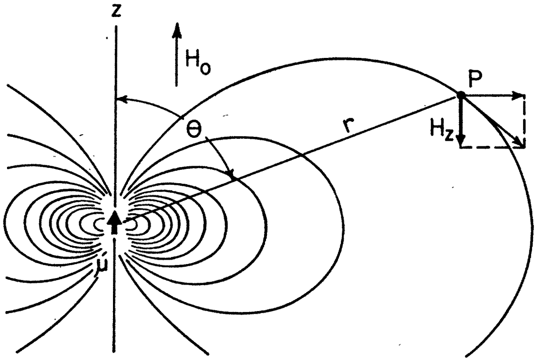

FIG. 4. The magnetic field from a dipole, μ, at a nearby point, P. The magnitude of the component, H_z, is (μ/r^3) $(3 \cos^2 \theta - 1)$, and the total field at P, in the z-direction, is $H_0 + H_z$. In the cases considered here, $H_z \ll H_0$.

This component of the local field at P is given by

$$(H_{loc})_z = \frac{\mu}{r^3}\,(3 \cos^2 \theta - 1),$$

where θ is the angle shown in Fig. 4. Thus the *total* magnetic field, in the z direction, that would be experienced by another proton located at P, is $H_0 + \frac{\mu}{r^3}$ $(3 \cos^2 \theta - 1)$. If the spin vector of the proton at the origin had been directed downward rather than upward (as we have seen, the states (+) and (−) are almost equally probable) the field at P would have been $H_0 - \frac{\mu}{r^3}(3 \cos^2 \theta - 1)$.

The "local field" term in each of these expressions amounts to a few gauss, if μ is the proton moment and r is a distance of the order of 10^{-8} cm, whereas the field, H_0, is ordinarily several thousand gauss. The effect of the neighboring protons is thus to alter slightly, either increasing or decreasing, the total magnetic field experienced by a selected proton, and we should expect the resonance condition, for that particular proton, to be modified accordingly to read:

$$\nu = 2\mu(H_0 + H_{loc})/h$$

where H_{loc} represents the instantaneous sum of the fields of all its neighbors. Only the nearest neighbors will contribute significantly to H_{loc}, because of the inverse-cube dependence and the angular dependence of the dipole field.

Although the picture which has been drawn is considerably oversimplified, the gravest omission being the neglect of the effect of the *precession* of the nuclear dipole, it can serve to explain the main features of the results shown in Fig. 4. Oddly enough, it is easiest to begin with the most complicated of the patterns, Fig. 3 (d), which has been observed and interpreted by Pake (*8*). The four components are observed in a single crystal of gypsum ($CaSO_4 \cdot 2H_2O$) when the crystal axis is oriented in a particular way with respect to the direction of the strong magnetic field, H_0.

The only important magnetic nuclei in gypsum are the protons in the molecules of water of hydration. The crystal structure of gypsum has been well established through the analysis of Wooster (*12*), but it will be recalled that X-ray diffraction yields no direct evidence of the location of protons in a crystal. Nevertheless, there is reason to assume that each proton has one near magnetic neighbor, the other proton belonging to the HOH molecule, and that the next nearest proton neighbor is considerably further away. If these more remote neighbors are ignored, the situation resembles that in Fig. 4; we have isolated interacting *pairs* of magnetic nuclei. Angle θ in Fig. 4 is now the angle between the H–H line in an HOH molecule and the magnetic field H_0. As it turns out, there are only two distinct H–H directions in a gypsum crystal; that is, for a given orientation of the single crystal in the magnet, θ has the same value for half the molecules in the crystal. From the protons in these molecules we should therefore expect a *pair* of resonance lines, symmetrically displaced to either side of the central position by an interval determined by μ, θ, and the interproton distance, r. (The doublet arises from the possibility of the partner being in either the (+) or (–) state.) The remainder of the molecules, to which a different value of θ applies, should give rise to another pair of lines, thus four lines in all. Each of these lines will be smeared out somewhat by the hitherto neglected fields of the more distant neighbors. This is just what is observed. Moreover, as the crystal is rotated in the apparatus, the separation of the components is found to vary precisely in accordance with the factor $3\cos^2\theta - 1$. From these observations, interpreted with the aid of a theory (*8*) more rigorous than we have given here, it is possible to determine not only the directions of the H–H lines with respect to the crystal axes, but also, with a precision of about 1%, the distance between the two protons in the HOH molecule—information which the X-ray analysis does not yield.

If the sample is a powder, rather than a single crystal, all possible values of θ will occur at once. A statistical analysis shows that the resulting superposition of many pairs of lines should yield the double-humped curve which is actually observed in this case (Fig. 3, c). A measurement of the hump separation again permits a determination of the interproton distance, but with less precision than before. The direction of the H–H lines in the crystal cannot be inferred in this case.

When each proton is surrounded by several equally near magnetic neighbors, no well-defined structure is observed. One finds instead a single broad line, the width of which, expressed in gauss, is of the order of magnitude, μ/r^3—hence, in general, several gauss. Such a situation is encountered in ice.

We have now to account for the extremely narrow line observed in water and other liquids. The essential difference is that the geometrical configuration of the molecule and its immediate environment can no longer be regarded as static. Instead, we must take into account the thermal motion of the molecule and its neighbors. The time during which the spatial orientation of a molecule of the liquid persists can be estimated from the molecular diameter and the viscosity of the liquid. In the case of polar liquids such as water, more direct evidence is provided by the dielectric dispersion; it will be recalled that the persistence of molecular orientation plays a central role in the Debye theory of polar liquids (*6*). In water at room temperature, this characteristic time is of the order of magnitude of 10^{-11} sec. In a time substantially longer than this, not only will the H–H line in a given molecule have tumbled into a new position, but the configuration and identity of the nearest neighbors will very probably have changed. The local field, H_{loc}, at the position of a given proton, is now a quantity which fluctuates in a random manner; the rapidity of fluctuation is very much higher than the resonance frequency for nuclear absorption.

It might be supposed that this rapid Brownian motion would completely obliterate the resonance phenomenon. On the contrary, the nucleus rides out the storm like a well-balanced gyroscope on perfect gimbals. In fact, a careful statistical treatment shows that the very rapidity of the fluctuations reduces their perturbing effect, the appropriate *average* value of H_{loc} being very much smaller than its instantaneous magnitude. The width thus predicted for the proton resonance in water is even smaller than that observed. The observed line width is caused by lack of perfect homogeneity in the field of the electromagnet.

If the viscosity of the liquid is increased, as by lowering its temperature, the local Brownian motion becomes less rapid, the perturbations due to the local field become *more* effective, and the absorption line broadens. Proceeding to the limit in this direction, the local motion is finally frozen out, and the line attains the width characteristic of a crystal. This whole range of behavior has been observed in glycerol, with results in quantitative agreement with the theory. Even in ice a certain amount of local motion persists well below the freezing point, as other lines of evidence strongly indicate (*9*), and the width of the proton line increases somewhat, with decreasing temperature, in the range - 5° C to - 40° C.

The nuclear resonance line width is thus a sensitive indicator, in some circumstances, of internal motion on a molecular scale. By this means, Bitter and Alpert and others at the Massachusetts Institute of Technology have recently investigated the so-called λ-point transitions in certain crystals. These transitions are marked by anomalies in the specific heat and have been attributed by various investigators to the more or less abrupt "freezing-in" of internal degrees of freedom associated with the rotation or oscillation of molecular groups. Solid methane, for example, displays a λ-point in the neighborhood of 20° K. Alpert (*1*) found that the width of the proton line in methane decreased markedly as the temperature of the solid was elevated through the λ-point and interpreted this as evidence for the activation of a *rotational* rather than a *vibrational* degree of freedom. In deuterated methane, which displays two λ-points, he found a similar behavior at the upper λ-point. Solid HCl and natural rubber were also investigated.

NUCLEAR RELAXATION

We return now to the question raised earlier: How are the nuclear spins brought into thermal equilibrium with the rest of the sample? It is seldom necessary to ask this question about an atomic or molecular system. A few interatomic collisions, occurring within 10^{-9} sec or so, suffice to bring about equilibrium. So thoroughly insulated is the nucleus, however, that in many substances *several seconds* are required for the populations of the levels (+) and (−) in Fig. 1 to adjust themselves into conformity with the Boltzmann factor. This time is called the thermal relaxation time of the nuclear spins. It is perhaps surprising to find a time so long associated with any atomic process; as a matter of fact, previous theoretical studies of this question had predicted even longer relaxation times than were observed. Two tasks were thus presented: (1) to measure the nuclear relaxation time in various substances under many conditions; (2) to devise an adequate theoretical explanation of the phenomenon. Although the problem is by no means completely solved, it is now possible to account rather satisfactorily for the relaxation effects observed in liquids and in a restricted class of solids (*5*). We can only indicate here the connection between nuclear relaxation and those features of the liquid or solid structure which have already been encountered in our discussion of line width.

Exchange of energy—that is, "thermal contact"—between the nuclear spins and their surroundings requires the existence at the nucleus of oscillating magnetic fields that (a) satisfy the resonance condition and are hence capable of inducing (+) → (−) and (−) → (+) transitions, and (b) originate in the thermal motion of the surroundings. Just such a mechanism is provided by the local Brownian motion which, as we have seen, causes a rapid and random variation of the local field produced by neighboring magnetic nuclei. One has to turn to the theory of random processes to compute the effective intensity, in the "spectrum" of the fluctuating local field, of the particular frequency required. One finds that the intensity is sufficient to explain the effects observed, and that a theory can be constructed which successfully accounts for the observed variation of nuclear relaxation time with the viscosity of the liquid.

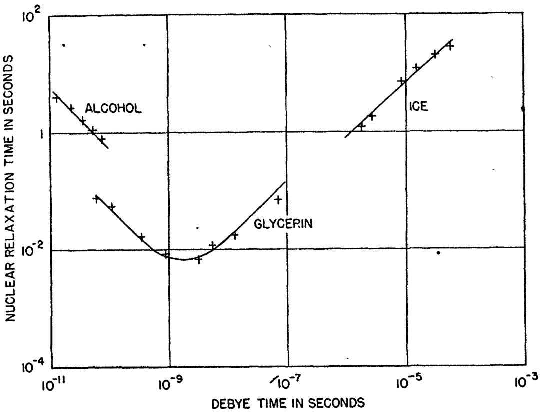

FIG. 5. The thermal relaxation time for protons in ethyl alcohol, glycerin, and ice, measured at 29 Mc/sec, plotted against the Debye relaxation time, obtained from dielectric dispersion data. Note the logarithmic scales. The slope of the solid lines for alcohol and ice and the shape of the solid curve for glycerin have been drawn in accordance with the theory.

Again, the important parameter is the characteristic time for reorientation of a molecule and redeployment of its neighbors, which, as noted earlier, is closely related to the characteristic time in the Debye theory of dielectric dispersion. In Fig. 5 the observed nuclear relaxation times, in ethyl alcohol, glycerin, and ice, are plotted against the "Debye characteristic time" obtained from published data on dielectric dispersion. Each of the points belonging to one of the curves was obtained at a different temperature. The curves are drawn in accordance with theory. The agreement is as good as one could expect, and it can be said with some confidence that the main features of the process of nuclear relaxation in these substances are understood.

So far as the structure of the substance is concerned, one learns from these curves only what could be learned from measurement of the resonance line width or, forgetting about the nucleus, from measurements of dielectric dispersion. However, the relaxation time can be measured even when the true line width is too small to be resolved, and the method applies equally well to nonpolar liquids which would not show dielectric dispersion.

One of the most interesting problems encountered in the study of nuclear relaxation is still unsolved. In many crystals the nuclear relaxation time appears to be much too short to be explained by any existing theory. The most striking evidence of the inadequacy of existing theories comes from the work of B. V. Rollin and collaborators at Oxford, who have investigated nuclear relaxation at very low temperatures (*11*). They report a relaxation time of the order of 5 sec for Li^7 nuclei in lithium fluoride, at a temperature of 2° K. The mechanism which brings about so rapid an exchange of energy between the nuclear spins and their environment, at this low temperature, is unknown. The thermal vibration of the nuclei in the crystal lattice, *even at room temperature,* is not violent enough to explain a relaxation time as short as this. It is difficult to imagine any other internal degree of freedom in a crystal of this type.

CONCLUDING REMARKS

Other lines of investigation, which could not be traced in detail here, have been followed far enough to suggest interesting applications of nuclear magnetism to problems of structure. The interaction between nuclear magnetic moments and the electronic magnetic moments of paramagnetic ions in solution, studied in a preliminary way by Bloembergen (*5*), depends upon the distance of closest approach of a magnetic ion to the nucleus in question, and hence upon the size and permanence of any complex surrounding the nucleus. R. V. Pound has very recently found evidence of interaction between the interatomic *electric* fields in a crystal and the electric quadrupole moment of a nucleus—a property of some nuclei which has been ignored in this article. It is too early to foresee the significance of this development.

To survey a field at such an early stage in its development is doubtless a rash venture. In the process of simplifying and condensing the statement of the problems, one runs the risk of creating an impression of tidiness which the actual state of affairs does not justify. More serious, perhaps, is the danger of exaggerating the importance of the information which the new techniques make available and the ease with which it can be obtained. On this last point, it should be said that the quantitative measurement of relaxation time and line shape is not easy. Nuclear resonance absorption is, after all, a feeble effect. The peak intensity of absorption in ice is such that a radio wave of the resonant frequency would be attenuated to half its amplitude only after traversing some hundred kilometers of solid ice. The data recorded in Fig. 5 were obtained from a sample weighing less than 1 gm. Despite this difficulty, I think we can look forward to the profitable development and extension of the field which these early experiments have opened.

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