Magnetic Resonance

PART II — MAGNETIC RESONANCE OF ELECTRONS

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Magnetic resonance of electrons is the analogue of magnetic resonance of nuclei, treated in the first part of this article. Though the analogy is close and the fundamental laws are identical, the two topics are remarkably different in detail. Though electrons are the commonest of particles, they display magnetic resonance only in somewhat exceptional cases. In many free atoms and most solid and liquid substances, magnetic resonance is suppressed by what is known as the "anti-parallel coupling" of electrons two by two. The exceptional cases are those of certain free atoms, ferromagnetic substances, and a restricted class of strongly paramagnetic substances; the resonance has also been observed very lately for the conduction electrons in metals. In the cases in which it does occur, resonance is likely to occur at a frequency or frequencies very different from that which the elementary theory predicts. This is sometimes because of the orbital motions of the electrons, oftener mainly because of the electric and magnetic fields existing in solids, and the deviations of the observed cases from the ideal case shed light upon these fields.

The subject of these pages is the magnetic resonance of electrons — "electron resonance" for short. Electrons being everywhere, one might expect it to be found in every substance; but for a fundamental reason it is a rare phenomenon, and this magnifies its interest. Those who search the literature for it under this its proper name will seldom find it, for it is frequently called "paramagnetic resonance" or, in appropriate cases, "ferromagnetic resonance." These are lengthy names which tend to veil the similarities between electron resonance and nuclear resonance, which latter was the theme of Part I of this article (in the January issue of this JOURNAL). I will introduce electron resonance by making use of all these similarities.

Magnetic resonance in general is due directly to the magnetism of

subatomic particles: nuclei and electrons. These, apart from the nuclei that are non-magnetic, may be visualized as minuscule barmagnets. The laws of resonance are determined by the fact that in a steady magnetic field, the magnetic moments of these particles may not point in any and every direction: instead, they are constrained to a finite and small number of what are called "permitted orientations." To each of these corresponds a special value of the energy of the little magnet in the field: thus the energy also is constrained to a finite and small number of "permitted" values. These are often called "Zeeman levels" or just "levels"; and the word "level" should be well known to those who are going to delve into the literature.
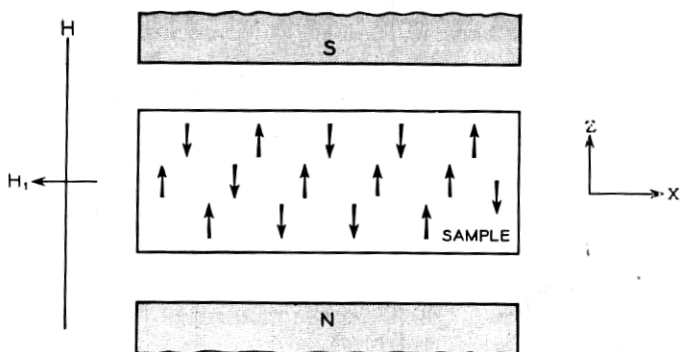

Fig. 1. — Scheme of the apparatus for observing magnetic resonance. The high-frequency circuits are omitted. The arrows within the sample may be taken as portraying the magnetic moments of either protons or electrons: their orientations are as given by the *old* quantum-theory.

Consider two orientations or levels of different energy-values. It will take *work* to turn the tiny magnet from the one of lesser energy to the one of greater energy. Magnetic resonance — and now I ought perhaps to speak specifically of magnetic resonance *absorption* — is such a turning. The agent of the turning and the source of the work is an alternating or oscillating magnetic field. The simplest cases are those in which the particle in question has only two permitted orientations. Many nuclei, among them the proton, belong to this class, and the electron belongs to it also. It is the analogy between proton and electron which I will develop.

Fig. 1 of this part is also Fig. 1 of Part I. The central rectangle depicts the *sample*, which for the study of proton resonance must be hydrogen or a compound thereof. The big arrow on the left represents a big magnetic field, of the order of several thousand gauss, which pervades the

sample; it is vertical and its strength is denoted by H. This is the field with respect to which the protons are oriented. These magnetic particles are represented by small arrows within the rectangle, the point of each arrow corresponding to the north pole of the corresponding proton. Slightly more than half of them are pointed in what I call the "up" orientation, which is that of lesser energy. The rest are pointed in the "down" orientation, that of greater energy. Magnetic resonance absorption of protons is the turning of "up" protons into the "down" direction.

The field which does the turning is an oscillating magnetic field with frequency (denoted by ν) in the radio-frequency range. It is horizontal, thus at right angles to the big field. It is produced either in a solenoid (the usual method for nuclear resonance) or in a resonant cavity (the usual scheme for electronic resonance) which encloses the sample but in Fig. 1 is left to the imagination of the reader.

Magnetic resonance occurs when the quantum-energy $h\nu$ of the oscillating field is equal to the work required to turn the proton from the up orientation to the down one:

$$h\nu = \text{work of turning} \tag{1}$$

h standing for Planck's constant. In Part I it was shown that the "work of turning" or energy-difference between the two orientations is equal to $2\mu_p H$: here μ_p stands for the magnetic moment of the proton, soon to be more carefully defined. Thus:

$$h\nu = 2\mu_p H \tag{2}$$

When ν and H are related by this equation one finds *proton resonance absorption*, which manifests itself by a splendid peak in the curve of absorption *versus* H for constant ν or the curve of absorption *versus* ν for constant H. For the frequency 42.6 megacycles the peak is found at $H = 10,000$ gauss.

To arrive at the basic formula for *electron resonance* we simply take (2) and substitute into it μ_e, the magnetic moment of the electron, for μ_p:

$$h\nu = 2\mu_e H \tag{3}$$

The magnetic moment of the electron is about 660 times that of the proton. Therefore if one works with such a field strength as brings the proton resonance into the radio frequency range, the electron resonance is to be sought in the microwave range. One might think that now I have said all that there is to be said about electron resonance; but this is only the beginning.

Much was said in Part I about the magnetic resonance of nuclei having more than two permitted orientations. We may seem to be wandering off the course if we revert to these, but this case is very pertinent.

There are nuclei with three, four, . . . up to ten or maybe more allowed orientations. One would expect them to display a multitude of peaks; but there is never more than one. This is for two reasons, which I give after introducing the symbol $(2I + 1)$ for the number of orientations. First, it is impossible to turn a nucleus from any orientation to any other *except* the nearest to the original one. This reduces the number of possible peaks to one fewer than the number of orientations. But second, all of these $2I$ possible peaks are of the same frequency for given H, or at the same field strength for given ν, so that they all coalesce into a single peak.

The formula for this apparent single peak which is strictly $2I$ coincident peaks has been derived in Part I, and this is it:

$$h\nu = (\mu/I)H \qquad (4)$$

Now it is necessary to interpret I and μ; and the interpretation is different according as one uses the old quantum theory or the new quantum mechanics. The old quantum theory deals more simply with these problems, and would be preferable if this field could be isolated from all the rest of physics; but the new quantum mechanics is worth the extra trouble that it causes.

In the old quantum theory, there are two definitions of I that reduce to the same thing. First, I is the angular momentum of the nucleus in terms of the unit $h/2\pi$; that is to say, the angular momentum of the nucleus is $Ih/2\pi$. Second, $Ih/2\pi$ is the maximum possible projection, upon the field-direction, of the angular momentum of the nucleus. This is because, among all of the allowed orientations of the nucleus, the one which is most nearly parallel to the field-direction is *exactly* parallel to the field-direction. So it was shown in Fig. 1.

In the new quantum mechanics, the second of these definitions remains valid and the first does not. This is because the orientation which is most nearly parallel to the field-direction is not exactly parallel thereto. It is inclined, in fact, to the field-direction by the angle *arc cos* $I/\sqrt{I(I + I)}$, and the angular momentum of the nucleus is $\sqrt{I(I + 1)}(h/2\pi)$.

Thus there is one definition of I which is valid under both theories, and that is, that I is the maximum possible projection upon the field-direction, of the angular momentum of the nucleus in terms of the unit $h/2\pi$. Similarly it is always correct to say that μ is the maximum pos-

sible projection upon the field-direction, of the magnetic moment of the nucleus. But since these phrases are intolerably long, one avoids them by saying that I is the spin and μ the magnetic moment of the nucleus. In this sense, which to the users of quantum mechanics is a distorted one, the words "magnetic moment" shall be used hereafter.

The spin of the proton is $1/2$, and so is the spin of the electron. Equation (4) degenerates into (3) for the electron and into (2) for the proton. These we had already; what was then the point of introducing here the general case?

Well, the point is that two, or three, or several electrons may collaborate in what is known as "parallel coupling," though in the new quantum theory it is not quite parallel. They behave as though they formed a rigid unit, of which the spin is the sum of their spins and the magnetic moment is the sum of their magnetic moments. Thus if there are N of these electrons welded together (metaphorically speaking) it comes to the same as though there were a single particle of spin N times $1/2$ and magnetic moment N times μ_e. On putting these values of I and μ into equation (4) we find ourselves right back at equation (3), which is that for the individual electron. There is a single peak of magnetic resonance composed of N coinciding peaks, and it is just where the peak for a single electron would be. Thus in the ideal case, N electrons coupled parallel behave just like one electron by itself.

Such a conclusion may seem hardly worth the trouble of arriving at it; but note the stipulation "in the ideal case." This refers to what has been tacitly but obviously assumed till now, to wit, that no force acts upon the electronic magnet except the big field H. But there are also what I will call "local forces," forces due to fields within the sample arising from other particles in the sample. These forces may, and they often do, separate the N peaks which in the ideal case coincide. Often one finds a flock of resonance lines where, or near where, there should be only one; and if this is the explanation (which is not always the case, for there are other causes of "splitting") then the number of lines in the flock is the number of electrons coupled parallel.

This illustrates one of the great contrasts between the electronic resonance and the nuclear. Nuclear resonance is a "textbook phenomenon." The ideal case and the actual case are close together; the deviations due to the local fields are neither trivial nor useless, but they are not large enough to distort the simple laws, and it is quite permissible to leave them out of a first presentation. But the phenomenon of electronic resonance is liable to be distorted almost beyond recognition; and if one were to present only the cases in which the local fields are negli-

gible in effect, one's story would be relatively short and it would be grossly inadequate. But here the physicist, true to the tradition of his science, turns hindrance into help, and analyzes the distortions for the knowledge they are capable of giving about the fields prevailing in the sample. Thus whereas nuclear resonance is largely used for getting light on nuclei, the electronic resonance is largely studied for the information that it yields about the solid state.

Another of the great contrasts is due to what are called the "anti-parallel couplings" between electrons. Generally speaking (and this means: conceding an occasional exception) any type of nucleus of non-zero magnetic moment will display a detectable resonance if there are enough of them in the sample. Were this so with the electron, every substance whatsoever would display electron resonance. Experience shows that electron resonance is rare, usually conspicuous by its absence.

This is because electrons may, and not only may but usually do, pair off with one another in such a manner that the spin of such an "anti-parallel" pair is zero and so is the magnetic moment. There is no resonance for such a pair; and the customary absence of electron resonance signifies that in most solids, all the electrons are joined two by two into antiparallel pairs (this was known before magnetic resonance was first produced). I will call such electrons "compensated"; in this language, the substances in which magnetic resonance is to be sought for are those with uncompensated electrons. Mostly these belong to one or the other of two classes: the ferromagnetic bodies including the anti-ferromagnetic, and the "strongly paramagnetic salts." But there are a few other cases, and among these are those which are closest to the (unattainable) ideal of the perfectly free electron subjected.

THE NEARLY IDEAL CASES

Nearest of all to the ideal case are presumably the atoms which contain uncompensated electrons and are available for study by the molecular-beam method. Outstanding among these is the hydrogen atom, whose single electron must remain uncompensated because there is no other in the atom. About or quite as good are the atoms of sodium, potassium, and the other alkali metals, each of which contains a single uncompensated electron not to speak of several which are compensated. Moreover, these atoms are normally in a "ground state" in which the uncompensated electron has no orbital angular momentum. This hints at a complexity which is not always without influence on electron resonance, and must be mentioned here at the price of a detour.

Going back to ancient theory, let us imagine an electron revolving with frequency f in a circular orbit of radius r. It is equivalent to a current ef running continuously in the circular loop. According to the old theorem of Ampere, its magnetic moment is equal to the area of the circle multiplied by the current-strength; but the current-strength is to be expressed in *electromagnetic* units, so that the magnetic moment μ equals $(e/c)f\pi r^2$. The angular momentum p is mr times the speed of the electron, and therefore equals $2\pi mr^2 f$. For the ratio of the two we find:

$$\mu/p = e/2mc \tag{5}$$

This is what has lately been miscalled the "gyromagnetic ratio," a name which was originally applied and ought still to be applied to its reciprocal. It would be good to follow Gorter's suggestion of calling it the "magneto-gyric ratio."

I now state equation (5) in another fashion so as to introduce a symbol which is really a word, and is *the* technical word of this field of physics: it ought to be a word all spelled out, but it is just the letter g.

$$(\mu_{\text{orb}}/p_{\text{crb}}) = g(e/2mc), \qquad g = 1 \tag{6}$$

Thus g is the ratio of magnetic moment to angular momentum given in terms of $e/2mc$ as unit, and *its value for the orbital motion of an electron is one*. Note also that though we have arrived at (6) in a very old-fashioned way, it is one of the results that have stood firm through all the mutations of quantum theory.

The study of what are known as "multiplets" in optical spectra led some thirty years ago to the conclusion that for the spin of the electron the magneto-gyric ratio is such that $g = 2$:

$$(\mu_{\text{spin}}/p_{\text{spin}}) = g(e/2mc), \qquad g = 2 \tag{7}$$

This belief was substantiated by the "Dirac theory," and was not upset until measurements were made of the magnetic resonance of electrons in atoms by the molecular-beam method. The first such measurements were made upon atoms containing uncompensated electrons which had orbital motion as well as spin. I pass them over, and come direct to the most recent experiments on hydrogen atoms in their ground state, where there is no orbital motion of the electron to complicate matters. These are so recent that they came into print as these words were being written.

The hydrogen atom is a good example to take, not only for the reasons that I have given already, but also because it may be compared with the hydrogen molecule H_2. The two electrons of the hydrogen *molecule* compensate one another, and there is no electron resonance. The two

nuclei — protons — of the molecule compensate one another in some of the molecules, enter into the parallel coupling in others. There are always some of these last in a beam of hydrogen molecules, and they produce the proton resonance of which so much was said in Part I. The *atoms* produce the electron resonance.

Look now again at equation (4), and remember that p is $Ih/2\pi$ — and remember that p is to be interpreted as the maximum permitted component, along the field-direction, of the angular momentum.

Consider now the experimenter with molecular beams of hydrogen *molecules* and hydrogen *atoms* at his disposal. In a magnetic field of field strength H he finds the proton resonance of the former at frequency ν_p, and ascertains (μ/I) of the proton by putting his data into equation (4):

$$(\mu/I)_p = h\nu_p/H \tag{8}$$

In the same field he finds the electron resonance of the latter at frequency ν_e, and ascertains (μ/I) of the electron similarly:

$$(\mu/I)_e = h\nu_e/H \tag{9}$$

Now he has both values; but the accuracy of both is contingent on the accuracy of the measurement of H, and this is not so good as he desires. However he can dispense with the measurement of H at a price — the price of getting his value of the magnetic moment of the electron in terms of units other than c.g.s. units. This is not a great sacrifice; Nature does not share our affection for c.g.s. units; there are others which are more suitable to the enterprises of the theorist.

If we divide (8) into (9) we get rid of both H and h. This means that if the experimenter measures ν_p and ν_e in one and the same applied field, he can evaluate (μ/I) for the electron in terms of (μ/I) for the proton without bothering about the values of H and h. Since I is the same for both particles, he obtains the ratio of the magnetic moments of electron and proton. The value of this ratio would be precious in itself, even if one had not the faintest idea of the value of either moment in c.g.s. units. It is 658.2288 ± 0.0006.

It is also feasible to get the value of (μ/I) for the electron in terms of the "unit" $eh/4\pi mc$. This entity is so important that it has a name of its own: it is called "the Bohr magneton."

There is also a combination of experiments by which $(\mu/I)_e$ may be evaluated in terms of the unit $(eh/4\pi mc)$. This unit is so important that it has a name of its own: it is called "the Bohr magneton." The reader can easily show for himself that (μ/I) in terms of this unit is none other than the quantity g, of which this is a second definition (not identical with that of g in Part I).

The frequency of the proton-resonance, ν_p, is compared in a special experiment with what is known as the "cyclotron frequency," ν_c, of the electron. A free electron, projected at right angles to a magnetic field H, describes a circle in the plane perpendicular to the field. The frequency with which it makes the tour of this circular orbit is given by the equation:*

$$\nu_c = 2(He/4\pi mc) \tag{10}$$

If this frequency is determined in the same field as has served or is to serve for the location of the proton-resonance, we have:

$$(\mu/I)_p = 2(eh/4\pi mc)(\nu_p/\nu_c) \tag{11}$$

and consequently:

$$(\mu/I)_e = 2(\nu_e/\nu_p)(eh/4\pi mc)(\nu_p/\nu_c) \tag{12}$$

So here is the value of (μ/I) for the electron expressed in terms of the Bohr magneton, determinable by measurements on ratios of frequencies only! At this point the reader may well wonder why I did not eliminate ν_p from (12) by simply dividing it out. The reason is that one group of experimenters has determined (ν_e/ν_p) at one fieldstrength and another group of experimenters has determined (ν_p/ν_c) at another fieldstrength, so that ν_p does not have the same value in the two brackets: this is trivial.

The old belief, as I remarked above, was that (μ/I) for the electron amounted to exactly two Bohr magnetons. But the combination of two experiments which I have just so sketchily described has led to the following result for the electron in the hydrogen atom:

$$(\mu/I)_e = g(eh/4\pi mc), \qquad g = 2.002292 \pm 0.000024 \tag{13a}$$

But is this truly the ideal case? Defining the "ideal case" as that of the free electron, remembering that the electron in the hydrogen atom is bound even though lightly bound, and making what is deemed the appropriate correction, one elevates the foregoing value of g by 35 parts in a million, and obtains:

$$\text{Ideal } (\mu/I)_e = g(eh/4\pi mc), \qquad g = 2.002327 \pm 0.000024 \tag{13b}$$

Thus the old belief was wrong by about one part in a thousand. Be it mentioned in passing that the Dirac theory which led to $g = 2$ has been modified in the meantime by what is known as "quantum electrodynamics", which gives a good account of this result.

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* To be derived by equating the force $Hv(e/c)$ exerted by the field upon the electron to the "centrifugal force" mv^2/r; here v stands for the speed of the electron and r for the radius of the circle.

Since I is $\frac{1}{2}$ for the electron (as it is for the proton) the magnetic moment of the free electron is:

$$\mu_e = (\tfrac{1}{2})g(e/4\pi mc) = 1.001146 \pm 0.000012 \text{ Bohr magnetons} \quad (14)$$

This is the value which is 658.2288 times the moment of the proton.

Another case very near to the ideal is afforded by the electrons of such atoms as manganese widely dispersed in a phosphorescent solid. Thus, there exists a measurement of g made upon "zinc sulphide phosphor" containing manganese atoms in a concentration of 0.001 per cent. The value is 2.0024 ± 0.0004. It must be said that the resonance in question is complicated both by fine structure and by hyperfine structure, terms to be explained in following sections. It is therefore necessary to use theory to locate, among the complex of peaks, the frequency which corresponds to the appropriate value of g.

Still another case which is close to the ideal is provided by the "F-centres" in colored crystals, mention of which was made in Part I. An F-centre is a cavity in a crystal lattice occupied by a free electron batting around, as I said in Part I, like a wild animal in a cage. Several physicists have found their resonance, present when the crystal is colored and absent when the crystal is bleached. One, who produced the coloration by neutron-bombardment, located the peak at $g = 2.00$. Others report 1.995 ± 0.001.

Still another case which is close to the ideal is afforded by the conduction electrons in a metal. These are so numerous that one might expect that the electron resonance that they produce must be extremely prominent. Yet the first such peak to be observed has been reported only as these lines are being written! The reasons for its inconspicuous character are two: most of the conduction-electrons are coupled antiparallel, and the skin-effect confines the oscillating field in a conductor to a very narrow region close up against the surface. The second of these hindrances is overcome by using a colloidal dispersion of the metal, of which the spherules are less than 10^{-3} cm in diameter. Data are available (though not yet all in print) for lithium, sodium and potassium. The values of g are within a few promille of 2.000; the differences between these and the "ideal" value are small but not trivial, and in the case of lithium have been explained.

ELECTRON RESONANCE IN PARAMAGNETIC SOLIDS

There are paramagnetic solids that display the electron resonance. A magnificent illustration is shown in Fig. 2, belonging to an organic

substance of which the name and the structural diagram are included in the figure. This is one of the strongest and sharpest electron-resonance peaks on record. The g-value is 2.0064 ± 0.0002; it is therefore *almost* an ideal case, but the difference from the ideal value is sure and significant. It would however be misleading to suggest that such a case is typical.

What are called the "strongly paramagnetic salts" form a group with several features in common. They tend to have long names, and they have complex chemical formulae; crystal lattices or at any rate unit-cells which are non-cubic; and atoms some of which belong either to the rare-earth elements or to the elements of the "first transition group," iron or cobalt for instance. These atoms are likely to have two or more uncompensated electrons in parallel coupling. I now recall what was said about such coupled electrons in the introductory passage.
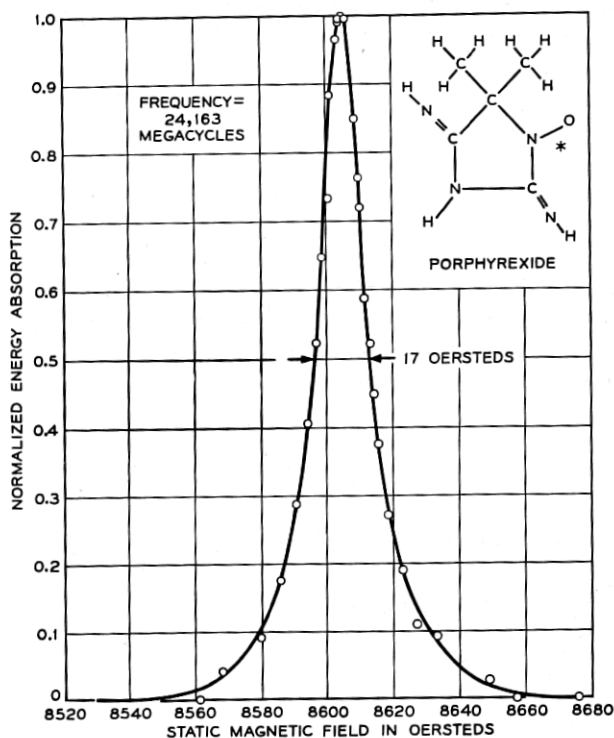

Fig. 2. — Electron resonance of porphyrexide. This is one of the strongest and sharpest peaks of electron-resonance yet observed. The g-value is 2.0064 ± 0.0002, which makes it slightly but significantly different from the ideal case. In the structural diagram, the asterisk signifies a three-electron bond. (A. N. Holden, W. A. Yaeger and F. R. Merritt).

Two or more electrons — N electrons, let me say — may form, in effect, a rigid unit having a total spin $S = N/2$ and a total magnetic moment $N\mu_e$. Such a unit will have $(N + 1)$ allowed orientations in the big magnetic field. These will engender N resonance-peaks. In the ideal case, all of these would have the same frequency $2\mu_e H/h$, and would therefore coalesce into a single peak at the position appropriate to $g = 2.0023$. But in these crystals we are likely to find cases far from ideal, because of the conjoined influence of two factors. These are the presence of *orbital* motions of the electrons, and the presence of a big electric field within the crystal.

Were the atoms in question free, we could allow for the orbital motions. There would be a single resonance-peak, corresponding to a value of g which could be computed by a formula well known and much used in optical spectroscopy. Incidentally, this formula was used in interpreting the earliest molecular-beam experiments (not here described) that were the first to show that g in the ideal case is not exactly equal to 2.

Now, however, we are dealing with resonating electrons that are in a strong electric field, and moreover, an electric field which is usually unsymmetrical. If the asymmetry is sufficiently great, the orbital motions suffer a singular effect. This effect is known as "quenching." It is impossible to explain and difficult even to describe without invoking quantum mechanics. One may say that the orbital angular momentum is no longer constant in time, and the associated magnetic moment almost but not quite disappears.

The spin survives the quenching: but it would not be right to say that the quenching restores the ideal case. The resonance is affected by what have been called the "remains" of the orbital magnetic moment. These have the following consequences:

(a) The N resonance-peaks, which coincide in the ideal case, may be drawn apart. They then form a group of N separate peaks, which is known as a "fine-structure pattern." The number N tells us the number of electrons coupled parallel in the atom, for these two numbers are the same. Often the number of electrons coupled parallel is known from independent evidence, and in such cases it is confirmed by the number of lines in the fine-structure pattern. Sometimes it is not otherwise known, and in such cases it is identified with the number N.

(b) The value of g corresponding to the centre of the fine-structure pattern may be altered considerably from 2.0023, falling as low as 1.35 or rising as high as 6.5. This is as though a part of the orbital magnetic moment were added to or subtracted from the magnetic moment of the spin.

(c) The value of g may depend upon the orientation of the applied magnetic field with respect to the crystal.

(d) The frequency of the resonance-peak or peaks may not be proportional to H. In fact, it may deviate so far from being proportional to H that extrapolation to $H = 0$ will indicate that even in the absence of an applied magnetic field there would be a separation of the levels. Thus the asymmetric electric field within a strongly paramagnetic crystal may by itself produce the effect, which hitherto we have been ascribing entirely to the applied magnetic field. This is called "zero-field splitting."

One sees only too well that the interior of a strongly paramagnetic salt is no place to look for the ideal case, and that resonance in such a salt is a theme for deep study and not for facile interpretation. As a matter of fact, electron resonance in paramagnetic salts is valued for its contribution to our knowledge of the electric fields in these crystals; which is to say, that it is a part of solid-state physics, the details of which lie beyond the scope of this article.

HYPERFINE STRUCTURE OF ELECTRON RESONANCE

One of the most beautiful phenomena in this province of physics — and, I venture to say, not in this province only but in the whole of physics — is the "hyperfine structure" or "hyperfine splitting" of the electronic resonance. Here we see the spin and the magnetic moment of the nucleus collaborating with those of the electron to produce an exquisite and lucid joint effect. It is still the *electronic* resonance, and must never be confused with the nuclear resonance; but the single resonance-peak of the ideal case is split into a group of peaks, the number of which is determined by the spin of the nucleus.

Fig. 3 relates to neodymium — not however to the metal, but to neodymium atoms in a salt of neodymium, diluted with a salt of another metal so that the neodymium atoms may not influence one another through undue proximity. Neodymium is an element with two "odd" isotopes — that is to say, isotopes of odd mass-number — and several "even" isotopes. The even isotopes have non-magnetic nuclei, and so do not perturb the electron resonance. Each of the two odd isotopes has a nucleus of spin 7/2 and non-zero magnetic moment. Such a nucleus will have eight permitted orientations in the big magnetic field. It will produce a local magnetic field in the region of the resonating electrons, and the strength of this field will depend on the orientation. The resonance-frequency depends on the big field compounded with the local field (we met with instances of this rule in the study of nuclear reso-

nance). Therefore there are eight resonance-peaks for the electrons in the atoms of the isotope 143, and eight more for the electrons in the atoms of the isotope 145. This is the key to the remarkable pattern shown in the curve at the bottom of Fig. 3.

In the middle of the pattern is the stump of a tall peak. This is the unperturbed peak due to the electrons in the atoms of even isotopes, those of which the nuclei have no magnetic moment. Whether it is at the position corresponding to $g = 2.00$ will depend on whether the displacement due to electric fields in the crystalline salt of neodymium, with which these data were obtained, is negligible or is not. Then, there are eight much shorter peaks. These are due to the electrons in the atoms
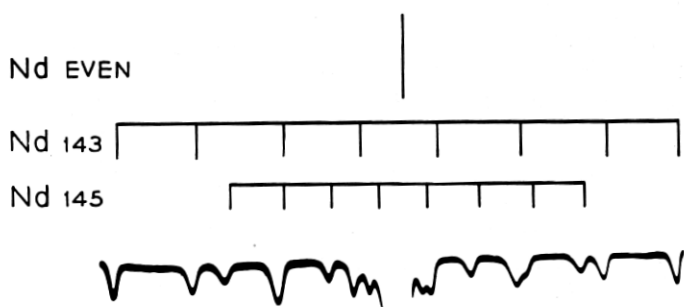

Fig. 3. — Hyperfine-structure pattern of the electron resonance of neodymium in a salt of the metal, showing that the nuclei of each of the odd isotopes of neodymium have eight orientations and therefore a spin of 7/2, and that the even isotopes do not affect the resonance. (Courtesy of B. Bleaney).

of the more abundant of the two odd isotopes. Then, there are eight still shorter peaks (provided we count one which is merged with one of the other group of eight). These are due to the electrons in the atoms of the less abundant of the two odd isotopes. This is beautifully confirmed by the fact that the statures of the two groups of peaks stand to one another in the ratio of the abundances of the two isotopes! Further, the spacings within the two groups stand to one another in the ratio of the magnetic moments of the nuclei of the two isotopes. As for the two combs that stand above the curves, they are markers to identify for the onlooker the members of the two groups of peaks.

Observations on the similar pattern of a (rare) isotope of vanadium — vanadium 50 — have led to the inference that this nucleus possesses a non-zero magnetic moment and a spin equal to 6 (the highest value so far known). This may seem surprising, since I have implied that nuclei of even mass-number have neither spin nor magnetic moment. Vanadium

50 is however a nucleus with an *odd* number of protons and an *odd* number of neutrons. Such nuclei, of which there are only a few stable examples, (in Part I we met with two, the deuteron and N^{14}), are not bound by the usual rule.

Ferromagnetic bodies owe their distinctive feature to uncompensated electrons. This suggests that the magnetic resonance of electrons will be discernible in such bodies, and so indeed it is. In this case it is commonly known as "ferromagnetic resonance." However, unless the sample is in the shape of a sphere, the resonance-peak will be found in what appears to be very much the wrong place. This is due to the magnetization of the substance, which produces a remarkable effect upon the location of the resonance. The field strength in the region occupied by the sample, which would be H if the sample were not there, is changed to a very different value; and yet in general it would not be right to take the value of H_i the "internal field strength" and put it in place of H in equation (3). We must understand this effect and make the proper allowance for it before we do anything else with the data (unless, I repeat, we confine ourselves to data obtained with spheres). The effect appears to be beyond the power of "intuition" to conceive, and we must have recourse to the fundamental equations, which describe the precession of the electronic magnets. It will be recalled that in Part I, we looked at nuclear magnetic resonance sometimes as the turning-over of nuclear magnets and sometimes as an outcome of precession. Now we are going to treat the electronic resonance as an outcome of precession.

The fundamental vector equation, which was given in a sort of diluted form as equation (6) of Part I, reads as follows:

$$dp/dt = \mu_e \times H_i \qquad (15)$$

Here p and μ_e stand for the angular momentum and the magnetic moment of the electron, and H_i for the field which operates on the electron. We have seen that μ_e/p is written as $ge/2mc$; we denote this quantity by γ; and we give it the minus sign because, for the electron, angular momentum and magnetic moment are antiparallel to one another. Now we have:

$$d\mu_e/dt = -\gamma\mu_e \times H_i \qquad (16)$$

This we proceed to write as three scalar equations; but first we replace μ_e by M. This will help to do away with the implication that the magnetic moment varies in magnitude (it is the *direction* that changes with

time) and will also convey the plausible suggestion that all of the resonating electrons in the substance are coupled parallel, so that M can signify the magnetization of the substance. We have:

$$dM_x/dt = -\gamma(M_yH_{iz} - M_zH_{iy})$$
$$dM_y/dt = -\gamma(M_zH_{ix} - M_xH_{iz}) \tag{17}$$
$$dM_z/dt = -\gamma(M_xH_{iy} - M_yH_{ix})$$

Now we are to make the following important substitutions, some of which are approximations.

(1) Presuming that M the magnetization of the substance will not deviate far from the z-direction, we are to write M for M_z.

(2) For H_{iz}, the z-component of the field actually operating upon the electrons, we are to write $(H - N_zM)$. Here H stands as heretofore for the applied field and N_z for the "demagnetizing factor" in the z-direction, which latter is a measure of the strength of the free poles on those surfaces of the sample which face the pole-pieces of the magnet (Fig. 1). Thus $-N_zM$ is the value of the field produced in the substance by these free poles.

(3) For H_{ix} and H_{iy} we are to write $-N_xM_x$ and $-N_yM_y$. This means that whatever applied fields there may be in the x and the y-directions are negligible, and yet the components of magnetization in these directions are not negligible, so that the free poles on the surfaces perpendicular to x and to y respectively are producing the internal fields of which $-N_xM_x$ and $-N_yM_y$ are the strengths.

(4) We are to ignore terms in which the product M_xM_y appears, these being small.

The fourth of these conditions makes dM_z/dt vanish: we are left with only two of the three equations (17), a convenience. Making the substitutions allowed by the first three conditions, we find that the other two assume the forms:

$$dM_x/dt = -\gamma M_y[H - (N_z-N_y)M]$$
$$dM_y/dt = -\gamma M_x[-H + (N_z-N_x)M] \tag{18}$$

Now suppose that M_x and M_y are periodic functions of time, of frequency ν. We write them as $M_x^0 \exp(2\pi i\nu t)$ and $M_y^0 \exp(2\pi i\nu t)$. Substituting into (18), we find:

$$2\pi i\nu M_x^0 + \gamma[H + (N_y - N_z)M]M_y^0 = 0$$
$$-\gamma[H - (N_z - N_x)M]M_x^0 + 2\pi i\nu M_y^0 = 0 \tag{19}$$

These two simultaneous equations will be compatible with one another — one might say that they make sense — only if they are ultimately the same equation. The ratio of the coefficients of M_x^0 and M_y^0 in the one must be the same as the ratio of the corresponding coefficients in the other. In words more natural to algebraists, the determinant of the coefficients must vanish. It turns out that this condition determines a specific value of ν, and this value is the resonance-frequency:

$$\nu = (ge/4\pi mc) \sqrt{[H + (N_x - N_z)M][H + (N_y - N_z)M]} \quad (20)$$

For reasons deriving from the history of celestial mechanics, this procedure is known as "solving the secular equation."

In the most common experimental set-up, the sample is a thin layer parallel to the z-direction — so thin that by comparison with its breadth, the free poles at the surfaces opposite the pole-pieces of the magnet may be regarded as infinitely far away. Under these conditions N_z vanishes, and so does N_x if we lay the x-axis parallel to the surface of the thin layer; but N_y does *not* vanish, it is in fact equal to 4π. Under the radical, the first factor becomes equal to H and the second to $H + 4\pi M$, which latter is by definition the induction B. We have:

$$\nu = (ge/4\pi mc) \sqrt{HB} \quad (21)$$

Note here that since B depends upon both H and M, one cannot use the formula unless one knows the value of M, which is the magnetization of the substance at saturation. This usually requires knowledge obtained from other experiments; but we shall meet with a case in which, at least "in principle," the value of B may be found from the resonance-experiment itself.

Equation (21) is the commonest formula for the ferromagnetic resonance, for it fits the "geometry" of the original and of most of the subsequent experiments. Yet there are other formulae corresponding to other geometries, and two of these are particularly important.

It is feasible to orient the layer at right angles to the big applied field. For this case we shall do well to turn the axis of z so that it remains parallel to the big field. Now N_x and N_y vanish and N_z becomes 4π, and the formula is this:

$$\nu = (ge/4\pi mc)(H - 4\pi M) \quad (22)$$

The quantity $(H - 4\pi M)$ is the internal field H_i, the field strength within the magnetized body. This is the special case in which the right result is obtained by going back to equation (4) and putting for H the actual field strength at the scene of the resonating electrons. In other

words, this is the special case in which the naive approach does not lead the student astray.

A more singular special case is that of the sphere. In this case N_x and N_y and N_z are all three of them equal — equal to one another but not to zero. Nevertheless the formula is just our old formula (3), the same as though there were no magnetization at all:

$$\nu = (\mu/I)(H/h) = (ge/4\pi mc)H \tag{23}$$

One wonders how long it would have been before anyone set up equations (18) and derived equation (21), if all experiments had been perfomde with spheres.

In the foregoing pages we have derived the resonance frequency by making certain listed approximations in the basic equations (19). Among these approximations was the neglect of the oscillating field, parallel to the axis of x. We arrive at some interesting results by introducing this field into the equations and giving it an arbitrary frequency, while continuing to make all of the other approximations. It shall be denoted by $H_1 \exp(2\pi i\nu t)$; H_1, it may be recalled, was the symbol used in Part I for the amplitude of this field. In this passage ν shall signify any frequency that the experimenter may choose to apply, while the resonance-frequency heretofore called ν shall change its symbol and become ν_0.

On the right-hand side of the second of the equations (19) will now appear, as the reader can show for himself, $-\gamma M H_1$ instead of zero. The two simultaneous equations now make sense for any value of ν, instead of just the value ν_0. On solving them for M_x^0, one finds:

$$M_x^0/H_1 = \frac{M}{H + (N_x - N_z)M} \frac{1}{1 - (\nu/\nu_0)^2} \tag{24}$$

The quantity on the left, and hence also the quantity to which it is equated, is the "susceptibility" of the substance with respect to this oscillating field which, be it remembered, is imposed at right angles to the big applied field.

The quantity on the right has the well-known form of an optical dispersion-curve. Suppose the frequency to be increased from zero. The susceptibility rises from a finite and non-zero value at $\nu = 0$ to positive infinity at the resonance-frequency ν_0; here it jumps suddenly to negative infinity, from which value it rises asymptotically to zero as the frequency is increased toward infinity.

In magnetics there are methods of measuring directly, not the susceptibility χ itself but the sum $(1 + 4\pi\chi)$, which is called the "permeability" and is denoted by μ. It is evident that while the susceptibility

is rising, with increase of frequency, from its negative-infinite value at ν_0 to its asymptotic value of zero at infinite frequency, the permeability is rising from negative infinity to an asymptotic value which is equal to $+1$. Somewhere along this range of frequencies it must pass through zero, at a frequency to be denoted by ν_i. For a stratum parallel to both the big applied field and the oscillating field, it is easily shown that ν_i is equal to $(ge/4\pi mc)B$. This offers a way of determining B and consequently M.
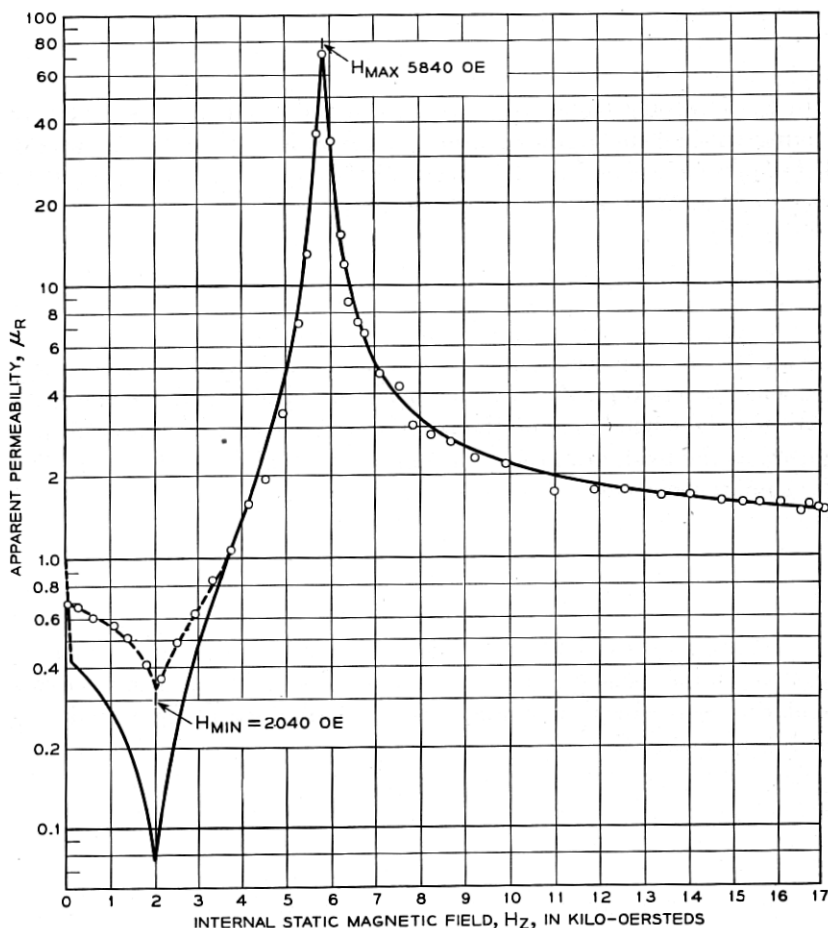

Fig. 4. — Ferromagnetic resonance in Heusler alloy (Cu-Mn-Al). "Apparent" permeability is plotted against H at constant frequency; the resonance-maximum (at the position corresponding to $g = 2.02$) is vividly shown, as is the minimum mentioned in the text. The solid curve is a theoretical curve based on a specific assumption about damping. (W. A. Yager and F. R. Merritt).

Next suppose that what is plotted against ν is not μ but $|\mu|$, the absolute value of the permeability. The portions of the μ-vs-ν curve which were below the horizontal axis now appear inverted and above the horizontal axis. The curve has an upward-pointing peak reaching to infinity at ν_0, and a downward-pointing peak touching the axis with its tip at ν_i.

Such is the general aspect of the curve of Fig. 4, pertaining to a Heusler alloy. There are superficial differences: the curve of Fig. 4 is plotted against H for constant frequency, and the scale along the axis of ordinates is logarithmic. The reader can easily make allowance for these. There is also a fundamental difference: the curve reveals the presence of damping or relaxation, which broadens the peaks and prevents $|\mu|$ from rising to infinity or dropping quite to zero. The continuous curve is derived from a theory which involves a specific assumption about the damping; one sees that it agrees well with the data excepting in a region around the minimum. Curves such as these are likely to be influenced by anisotropy in the ferromagnetic substance, which reversely can be evaluated from the curves.

How about the values of g for ferromagnetic substances? The Heusler alloy to which Fig. 4 pertains has a value of g which, so far as the accuracy of the experiment permits us to judge, may be identical with the ideal value (the most probable value is however 2.01). This is an exception and not the rule. The range of values is rather wide, though apparently not so wide as in the strongly paramagnetic salts. Most of them lie between 2.22 (for cobalt) and 2.01 (for the Heusler alloy aforesaid); but there are instances of values still higher, including one of 3.75 for manganese arsenide. There is also at least one value lower than 2.00; it is presented by gadolinium, a very interesting element. Below its Curie point at 16° absolute, gadolinium shows a resonance-peak of which the breadth interferes with a precise location of its top; the value of g is given as 1.95 to 1.96. Above the Curie point, gadolinium is paramagnetic, but the peak persists and is sharper; the value of g is 1.95 $\pm$ 0.03. I remind the reader that when the experiment is such that formula (21) must be used, a g-value implies an assumption about the value of M the magnetization of the substance at saturation.

I must not close this topic without alluding to something which there is not space to expound. Experiments on the "gyromagnetic effect" — something which has a much longer history than ferromagnetic resonance — lead to values of a quantity which has also been denoted by g. Until a few years ago it was supposed that this quantity must be the same as the g of these pages; but experiment has ruled otherwise, and theory has been successful in at least suggesting a reason. The g of these

pages is now called the spectroscopic splitting factor; the other has been set apart as the "gyromagnetic" g, and some people have even taken to writing it as g', which seems rather unfair to the senior g. It seems to be a general rule that when one of the two is greater than 2.00 the other is smaller than 2.00; and in the case of the Heusler alloy, they may well coincide.

ACKNOWLEDGEMENT

REFERENCES

This makes no pretense of being a bibliography of magnetic resonance: such an enterprise would cover more pages of this Journal than these articles themselves. It is somewhat, but not much, more than a listing of the sources of the data quoted in the articles, with the names which have been omitted in the belief that names tend to slow down exposition. Many relevant papers, with an abundance of footnote references to anterior work, are to be found in what I abbreviate by P.I.C.S.R. ("Proceedings of the International Conference on Spectroscopy at Radiofrequencies, Amsterdam, 1950" separately published and also printed as part of Volume 17 of *Physica*).

The *locus classicus* for the nuclear resonance absorption is the paper of Bloembergen, Purcell and Pound (*Phys. Rev.* **73**, p. 670, 1948); the first publication of this school is by Purcell, Torrey and Pound in *Phys. Rev.* **69**, p. 37, 1946. The *locus classicus* for the precession-theory and the nuclear-induction method is the paper of Bloch (*Phys. Rev.* **70**, p. 460, 1946), followed by the first lengthy description of nuclear-induction measurements by Bloch, Hansen and Packard (*ibid.* p. 464); the first publication of this school is in *Phys. Rev.* **69**, p. 127, 1946. The discovery of nuclear magnetic resonance by the molecular-beam technique was disclosed by Rabi, Zacharias, Millman and Kusch in *Phys. Rev.* **53**, p. 318, 1938, and a more detailed account is given *ibid.* **55**, p. 526, 1939; consult also the paper of Kellogg, Ramsey, Rabi and Zacharias *ibid.* **57**, p. 677 (1940) for the resonances of protons and deuterons in molecular beams of H_2, D_2 and HD.

The reference to the article of G. E. Pake (*Am. Jour. Phys.* **18**, pp. 438–452 and pp. 473–486, 1950) is here repeated to draw attention to this excellent survey of nuclear magnetic resonance and relaxation. Another survey article is that of Rollin, *Reports on Recent Progress in Physics*, 1948–49. The reference for the chemical shift in ethyl alcohol (Fig. 7 of Part I) is Arnold, Dharmatti and Packard, *J. Chem. Phys.* **19**, p. 507, 1951. For the influence of F-centres on nuclear relaxation-time see Hatton and Rollin, *Proc. Roy. Soc.* **198**, p. 231, 1949.

For the final experiments on determination of g for electrons in hydrogen atoms see Koenig, Prodell and Kusch (*Phys. Rev.* **88**, p. 191, 1952); references to earlier

work on other atoms are listed there. For the determination of the proton moment see Gardner, *Phys. Rev.* **83,** p. 996, 1951, and Sommers, Hipple and Thomas, *ibid.* **80,** p. 487, 1950. For the measurement of g with F-centres see Hutchinson and Noble, *ibid.* **87,** p. 1152, 1952, and Tinkham and Kip. *ibid.* **83,** p. 657, 1951, and Schneider and England in P.I.C.S.R.; this last is also the source for the work ion zinc sulfide phosphor. For resonance of conduction-electrons see Griswold, Kip and Kittel, *Phys. Rev.* **88,** p. 951, 1952, and papers yet to be published.

The resonance-peak of Fig. 2 of Part II of this article, for porphyrexide, comes from Holden, Yager and Merritt, *J. Chem. Phys.* **19,** p. 1319, 1951. The literature of resonance in strongly paramagnetic salts is extensive and tough; I refer to the papers in P.I.C.S.R. and the references they give. The basic theory is to be found in the book of J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford, 1932).

Hyperfine structure of electron resonance was discovered by the late R. P. Penrose (see *Nature,* **163,** pp. 988 and 992, 1949). This field is almost a monopoly of Britain and in particular of Oxford; many of the papers bear the name of Bleaney with or without collaboratores. Fig. 3 of Part II of this article comes from *Proc. Phys. Soc.* **63,** p. 1369, 1950; the statements about vanadium 50 from *ibid.* **65,** p. 952, 1952.

The discoverer of ferromagnetic resonance was J. H. E. Griffiths (see *Nature,* **158,** p. 670, 1946). The precession-theory for ferromagnetic substances is due to Kittel; equation (21) of this article is derived in *Phys. Rev.* **71,** p. 270, 1947; a fuller treatment appears *ibid.* **73,** p. 155, 1948. Survey articles are those of Van Vleck in P.I.C.S.R. and Kittel in *Jour. de Phys.,* **12,** p. 291, 1951. Fig. 4 comes from the paper of Yager and Merritt, in *Phys. Rev.* **73,** p. 318, 1949; a similar curve for supermalloy appears in the preceding paper; references to the g-values of other ferromagnetic substances are given by Yager. The question of "g versus g'" is discussed by Kittel in *Phys. Rev.* **76,** p. 743 (1949).