THE OVERHAUSER EFFECT IN SOLIDS

by

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PREFACE

The work described in this thesis was started late in 1953. It had occurred to me that nuclear physics could be greatly helped by some co-operation from the field of solid state. In nuclear physics one has to bear in mind the spin of the nucleus in attempting to account for many experimental results. In many of the experiments where nuclei are scattered off other nuclei the target nucleus may be in any one of a number of initial m-states or orientations of this nuclear spin. If the solid state physicist could arrange to have the nuclear spin held predominantly in one such state the interpretation of the results would be greatly simplified for the nuclear physicist, and the amount of information obtainable in a scattering experiment would be increased. In particular, it was felt that a major contribution to the understanding of nuclear forces could be made if a scattering experiment was carried out in which polarised protons were scattered off polarised protons. The production of partially polarised beams of protons has been accomplished. The production of a polarised proton target, on the other hand, is a much more difficult problem. It was an interest in this ideal which brought me into the field of solid state. Dr S.C.Curran F.R.S. encouraged me in the early stages and took an active interest in this problem up to the time of his leaving the department.

As this field was entirely new to me a study was made of the literature, the information gleaned from which has been reviewed in Part I of the thesis. It soon became evident that the technique of nuclear magnetic resonance would be a valuable tool for studying the degree of nuclear polarisation. A number of first class review articles, notably by Pake in the American Journal of Physics (1950) and by Pound in the Progress of Nuclear Physics (1952), are available on the subject of nuclear magnetic resonance. For this reason it was considered unnecessary to include a re-iteration of these comprehensive articles and only a brief review of this subject is given.

Of all the techniques of nuclear polarisation discussed in the review the method suggested by

Overhauser appeared to me to be the most promising. The experimental and theoretical results which have been published on the Overhauser Effect, as it is called, have been discussed in the latter half of Part I. I concluded that a valuable contribution could be made to this field if the theoretical results could be extended to complex crystalline solids.

In Part II a theoretical treatment is given of the problem in the solid state. The treatment is a generalisation of one given by Solomon of a much simpler system. The treatment is original.

In Part III a description of the experimental apparatus is given. A detailed account of each circuit is not given because this is readily available in any one of the books or review articles on nuclear magnetic resonance. (Andrews, 1955; Pake, 1950; Pound, 1952). I built all the electronic apparatus with the exception of the power supply of the large magnet. For this I was responsible for its design, layout and completion. The metal work and wiring were done for me by Mr R.McKinnes for which I wish to thank him. Throughout this work I have been greatly helped by advice from Mr T.Pollok and Mr J.Lindsay of the electronic shop. I wish to thank them for this and the workshop staff for constructing the box used for the radiofrequency bridge. Mr S.Hamilton and Mr A.Trotter I wish to thank for designing and constructing the second gearbox which was used for the slow magnetic field sweep of the large magnet.

The experimental results are given in Parts IV and V. These results are the first ever reported of the nuclear Overhauser effect in solids. I have been responsible for their interpretation.

The work is concluded in Part VI. The suggestions made here are original. In the case of the optically induced nuclear polarisation the technique is the same as that due to Kastler. Its application to organic phosphors, however, is to the best of my knowledge, original.

I wish to thank Mr R.Azuma and the members of the solid state group for many valuable discussions and helpful criticism. Dr G.A.P.Wylie I wish to thank for the interest he has taken in this work

and for many helpful suggestions and criticism. I wish to thank the Shell Petroleum Company for a Scholarship to the United Kingdom. I am indebted to the University of Glasgow for a Research Fellowship. I wish to thank Professor P.I.Dee for making available to me the excellent facilities of the Department of Natural Philosophy.

All the work of this thesis was done without supervision and unless otherwise stated is claimed to be original.

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1. INTRODUCTION

1.1 Nuclear Magnetism

In 1925 Uhlenbeck and Goudsmit pointed out that the interpretation of atomic spectra could be simplified if it was assumed that the valence electron possessed 'spin'. They assumed that the projection of this spin angular momentum on any axis could have only two values $\pm \frac{1}{2}$. Owing to its charge the electron could be expected to generate a magnetic moment which would couple to the magnetic field of other electrons and so modify the energy levels of the atom. Pauli (1924) ascribed a similar property to the nucleus in order to account for the hyperfine structure of atomic spectra. However, it was found that the nuclear spin, I, for different nuclear species could have many different values. These values range from 0 to 7 for the stable isotopes in the Periodic table. The nucleus also possesses a magnetic moment. This magnetic moment is different for each nuclear species but is given to an order of magnitude by the nuclear magneton $e\hbar/2Mc$, where M is the mass of the proton. Recent advances in technique have made it possible to measure the spins and magnetic moments of a great many nuclei. Spectroscopy has been extended to the radio frequency end of the spectrum and it has now become possible to detect the effects of the nuclear magnetism of matter in bulk.

1.2. Nuclear Magnetism of Matter in Bulk.

Matter which is otherwise diamagnetic shows a very weak paramagnetism if the nuclei of which it is composed possess a magnetic moment. Lasarew and Schubnikow (1937) were able to measure the magnetic moment of the proton by a measurement of this paramagnetism in solid hydrogen. In 1936 Gorter pointed out that a radio-frequency method should make it possible to measure much more accurately the magnetic moments of nuclei. Through an unfortunate choice of materials he was unable to demonstrate the technique experimentally. It was not until 1945 that a successful experiment on these lines was carried out.

If a nucleus is placed in a magnetic field along the z-direction each of the sub-levels,m, which correspond to the 2I + 1 different projections of the total spin I on this direction will have different energies. The energy of each level is given simply by $m\mu H/I$, where μ is the maximum measurable value of the magnetic moment. In a large group of these nuclei each of the levels will have, initially, the same population. However, owing to their different energies they will eventually re-arrange themselves so as to be in thermal equilibrium with their environment. When this situation has been reached the population of each level 'n' will be given by the Boltzmann expression :

$$n = N \frac{e^{-\frac{m\mu H}{IkT}}}{\sum_{m}' e^{-\frac{m\mu H}{IkT}}} \qquad \ldots \quad 1.1.1,$$

where N is the total number of nuclei, k is the Boltzmann constant and T the absolute temperature. The energy $m\mu H$ is usually small compared to kT for the fields and for the temperatures that can be produced in the laboratory. Thus there is only a very small difference in population between the different m-states of the nucleus.

Gorter (1936) suggested that a radio-frequency radiation field of a frequency ν where

$$\nu = \frac{\mu H_0}{h I} \qquad \ldots \; 1.1.2,$$

would cause transitions between these sublevels. The probabilities of absorption and induced emission are the same, but owing to the difference of population of adjacent levels, a nett absorption of energy from the radiation field takes place. In 1945 Purcell, Torrey and Pound and , independently, Bloch, Hansen and Packard successfully performed an experiment on these lines. Purcell et al detected the additional loss in a resonant cavity due to the absorption of energy by the protons in paraffin wax as the magnetic field was varied. Bloch used a slightly different technique to detect the proton resonance in water. Since these early experiments much work has been carried out to study the immediate neighbourhood of the nuclei in matter.

The equation 1.1.2. shows that the peak of absorption occurs for the field H_0 at the nucleus. This field may differ from that of the applied field owing to the presence of other nuclei possessing a magnetic moment or owing to the diamagnetic shielding of the electron cloud. These effects have made it possible to elucidate many interesting phenomena in the gaseous, liquid and solid phases. (Pound, 1952; Pake, 1950)

The nuclear physicist has been primarily interested in the magnitude of the magnetic moments for the different species of nuclei. Another feature which is of interest to him occurs in experiments in which nuclei are scattered off other nuclei. In these experiments a beam of particles is accelerated to a known energy and then allowed to strike a target containing suitable nuclei. A study of the distribution of the scattered particles gives one information about the nuclear states of the bombarded nuclei. However, owing to the fact that all the sub-levels of the ground state of the nucleus are almost equally populated, one merely obtains an average over the different orientations of the target nuclei. More could be learnt about the nuclear forces if the target nuclei could be held in certain specified orientations or m-states. In recent years a number of methods have been proposed to make this possible.

1.3. Nuclear Spin Orientation

The different methods which have been put forward may be conveniently classified as static or dynamic methods.

Static Methods

(a) Direct Interaction

The obvious method of orienting a nuclear system would be to apply a sufficiently large magnetic field at a temperature such that the difference of energy between adjacent m-states would be comparable to kT. An appreciable difference of population would then occur once the material reached thermal equilibrium (Gorter, 1934). One would require magnetic fields of the order of 50,000 gauss and temperatures near 0.001 °K. While these magnitudes are not unattainable they do require very special techniques. Furthermore, at these temperatures the time for thermal equilibrium to be attained in some materials would be very long i.e. of the order of days. A further experimental difficulty is introduced by the presence of a very large magnetic field in the scattering chamber. For the above reasons no successful experiment on these lines has been reported.

(b) Paramagnetic Ion.

In certain paramagnetic ions the nucleus may lie in a magnetic field of the order of 10^5 to 10^6 gauss due to the electrons of an unfilled shell. At temperatures of 0.01 ^{o}K a comparatively small field of about 100 gauss would be sufficient to align the spins of the electrons in this shell. An appreciable alignment of the nuclear spin would then take place in the large internal field of the ion. (Ambler et al, 1953). Ambler and his colleagues have described a successful experiment using this method. Again this type of experiment requires rather special low temperature techniques. The use of the continuously operating magnetic refrigerator described by Daunt, Heer and Barnes (1953) might make this method more practicable.

(c) Quadrupole Interaction.

Nuclei which possess a spin which is greater than ½ will possess an electric quadrupole moment. In certain crystals the energy of interaction of this quadrupole moment with the gradient of the electric field at the nucleus is comparable with kT at temperatures near 0.01 °K. Due to the symmetry of the quadrupole moment a difference in population will occur only between states of different $|m|$. Spatial alignment of the nuclei can then be achieved by orienting a single crystal having axial ~~cylindrical~~ symmetry. Pound (1949) suggested this technique.

(d) Magnetic Anisotropy

In some paramagnetic crystals the internal magnetic field is strongly anisotropic. At temperatures at which the energy of interaction of the nuclear magnetic moment with these fields is comparable with kT a spin polarisation will take place along certain crystal axes. Orientation of a single crystal will then orient the nuclear spin. (Daniels et al, 1951). The disadvantage of the last two techniques is that one requires single crystals of the material containing the required nucleus. One would also have to know the magnitude and orientation of the internal fields of the crystal. For many nuclei it might be impossible to grow suitable single crystals. It is obvious that these two methods are not universally applicable.

Dynamic Methods

The above techniques depend for their success upon the attainment of thermal equilibrium in a system in which the energy difference between m-states is comparable to kT. The dynamic methods depend for their success upon the attainment of a steady state which is not one of thermal equilibrium.

(a) Kastler's Optical Method

Kastler (1950) has proposed a technique in which orientation of the nucleus is attained through the absorption of optical radiation.

Consider an atomic system which has a ground state $^1S_0$ containing two nuclear states due to the nucleus having a spin $\frac{1}{2}$. Let radiation which is circularly polarised in the positive sense along the z-direction be absorbed by the atomic system. Transitions will occur as shown in figure 1 from the $^1S_0$ ground state to the $^3P_1$ excited state.

From the excited state $+\frac{1}{2}$ transitions can occur in which m changes by 0 or -1. From the excited state $+\frac{3}{2}$ only transitions to the state $+\frac{1}{2}$ can occur. Transitions from the ground state to $-\frac{1}{2}$ or -3/2, in the excited state do not occur. Thus the atomic nuclei are "pumped" from the spin $-\frac{1}{2}$ via the $^3P_1$ $+\frac{1}{2}$ excited state to the spin $+\frac{1}{2}$ state. Radiation which is polarised in the opposite sense would pump the spins in the opposite direction. A successful experiment on these lines has been carried out on an atomic beam of sodium atoms. (Hawkins, 1953).

No successful experiment using matter in the solid state has been reported. In the solid state it is important that the nuclei should be pumped over faster than they can return by interaction with the lattice. At low temperatures where the lattice motion is greatly reduced it might be possible to maintain an appreciable difference in the population of the various m-states of the nucleus. A very intense light source and an efficient optical system would be required for this technique.

(b) The Overhauser Effect

In 1953 Overhauser predicted, on theoretical grounds, that in a metal a polarisation of the nuclear spins would occur if the spin levels of the conduction electrons were saturated by a strong radiation field. Bloch (1954) and Korringa (1954) soon showed that a similar effect should occur in any paramagnetic material. For a given temperature and magnetic field the nuclear polarisation should be enhanced by a factor of about a thousand over the value obtained in thermal equilibrium. In this technique it would be necessary to use magnetic fields of about 10,000 gauss, temperatures of 2°K and microwaves of 1 cm wavelength in order to achieve a 50% polarisation of the nuclear spin. It would be necessary to provide something like 10 watts of radio-frequency power at this wavelength in order to saturate the electron spin levels in a metal. This appears to be one of the most promising techniques for the production of polarised nuclear targets. It will be considered more fully in the next section.

1.4. THE OVERHAUSER EFFECT

Since Overhauser's original paper was published a number of treatments of the effect have been given. (Brovetti and Cini, 1954; Korringa, 1954;

Abragam, 1955). In order to understand the physical reason for the effect the treatment given by Brovetti and Cini is, perhaps, the most clear. It will be followed here.

The Scalar Interaction

In a metal the Hamiltonian which describes the magnetic interaction of the conduction electrons and the nuclei may be written in the form :

$$\mathcal{H} = -\frac{8\pi}{3}\mu_e\mu_I(\bar{I}.\bar{S})\,\delta(r) \qquad \ldots\ 1.4.1,$$

where μ_e is the magnetic moment of the electron, μ_I is the magnetic moment of the nucleus and $\delta(r)$ is the Dirac delta function of the relative coordinate of the electron and the nucleus (Korringa, 1950). The operators $\bar{I}.\bar{S}$ may be re-written in the form :

$$\bar{I}.\bar{S} = I_zS_z + \tfrac{1}{2}(I_+S_- + I_-S_+) \ \ldots\ 1.4.2,$$

where the operators $I_+ = (I_x + iI_y)$, ... etc have been introduced.

The first operator in 1.4.2 does not connect states of different I_z. The second term gives rise to transitions in which the electron goes from the state $+\frac{1}{2}$ to the state $-\frac{1}{2}$; and the nucleus from the state $-\frac{1}{2}$ to the state $+\frac{1}{2}$.

It has been assumed that the nucleus has a spin of $\frac{1}{2}$. The third term in 1.4.2. accounts for the reverse transition.

Let the population of the electrons in the state $+\frac{1}{2}$ be N_+ and the population of the electrons in the state $-\frac{1}{2}$ be N_- . Similarly, let the population of the nuclear states $\pm\frac{1}{2}$ be repectively $M_\pm$.

When the system has reached a steady state the equilibrium populations may be determined from the Law of Mass Action (Saha and Srivastava, 1935).

$$\frac{N_- \; M_+}{N_+ \; M_-} = K \qquad \ldots \; 1.4.3,$$

where K is obtained by integrating the Van't Hoff equation :

$$\frac{d \log K}{dT} = \frac{\Delta U}{RT^2} \qquad \ldots \; 1.4.4.$$

ΔU is the change of the internal energy of the system during the process $I_+ S_-$. Therefore:

$$\Delta U = -2H \; (\mu_e - \mu_I) \, \eta \qquad \ldots \; 1.4.5,$$

where H is the applied magnetic field and η is Avogadro's number.

Using the relation 1.4.5. in 1.4.4. one

obtains from 1.4.3.:

$$\frac{N_- M_+}{N_+ M_-} = \exp\left[\frac{-2H(\mu_e - \mu_I)}{kT}\right] \quad \ldots 1.4.6.$$

The constant which is required after the integration of 1.4.4. is obtained from noting that at very high temperatures $N_+ = N_-$ and $M_+ = M_-$. In thermal equilibrium two additional conditions of equilibrium must be satisfied, viz:

$$\frac{N_-}{N_+} = \exp\left[\frac{-2H\mu_e}{kT}\right] \text{ and } \frac{M_-}{M_+} = \exp\left[\frac{-2H\mu_I}{kT}\right] \quad \ldots 1.4.7.$$

If the system is irradiated with microwaves of frequency $2H\mu_e/h$ transitions occur between the $+\frac{1}{2}$ and the $-\frac{1}{2}$ states of the electron spin system. If the irradiation is very intense the two states will have their populations equalised i.e. $N_- = N_+$

Inserting this in equation 1.4.6. one obtains the ratio :

$$\frac{M_+}{M_-} = \exp\left[\frac{-2H(\mu_e - \mu_I)}{kT}\right] \quad \ldots 1.4.8.$$

Thus the nuclear polarisation at a given value of H and T is the same as one would find if the magnetic moment of the nucleus was $(\mu_e - \mu_I)$ instead of μ_I. For the proton this would amount to an increase of the polarisation by a factor of about 600.

Brovetti and Cini claimed that a similar nuclear polarisation should be obtainable in any paramagnetic material. This would be true if the electron-nuclear interaction could be described by a Hamiltonian of the form 1.4.1. However, unless the nucleus lies with the electron cloud distributed about it spherically, the correct Hamiltonian will be of the dipole-dipole form :

$$\mathcal{H} = \frac{\mu_e \mu_s}{r^3}\left(\bar{I}.\bar{S} - \frac{3(\bar{I}.\bar{r})(\bar{S}.\bar{r})}{r^2}\right) \quad \text{... 1.4.9,}$$

which may be expanded to give : (Andrews,1955, p.229).

$$\begin{aligned}\mathcal{H} = \frac{\mu_e \mu_s}{r^3}\Big[\Big\{ & I_z S_z - \tfrac{1}{4}(I_- S_+ + I_+ S_-)\Big\}(1 - 3\cos^2\theta) \\ & - \tfrac{3}{2}(I_+ S_z + I_z S_+)\sin\theta\cos\theta e^{-i\phi} - \tfrac{3}{2}(I_z S_- + I_- S_z)\sin\theta\cos\theta e^{+i\phi} \\ & - \tfrac{3}{4} I_+ S_+ \sin^2\theta e^{-2i\phi} - \tfrac{3}{4} I_- S_- \sin^2\theta e^{2i\phi}\Big] \end{aligned} \quad \text{... 1.4.10}$$

In this case a number of other transitions can occur apart from those given by equation 1.4.2.(e.g. The operation $I_+ S_z$ allows I_z to change while keeping S_z fixed. $I_+ S_+$ allows I_z and S_z to increase simultaneously.) These different processes compete with one another. The probability for each to occur must be computed in order to calculate the Overhauser effect. A similar treatment to the above could be given to obtain the resulting nuclear polarisation under these conditions. However, the treatment given by Solomon (1955) of the relaxation processes in

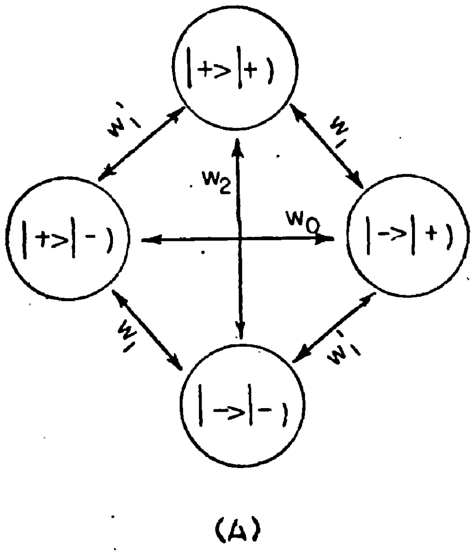


Figure 2

a system of two spins is more informative and gives a good starting point for a generalisation to more complicated systems.

The Dipole-dipole Interaction

The Hamiltonian describing the interaction of two particles I and S is given by the expression 1.4.9 or 1.4.10. Again only spin $\frac{1}{2}$ particles will be considered. Let the pair be placed in a magnetic field H along the z-direction. Let the Zeeman interaction energy of the particles with the field be large compared to the spin-spin interaction. Then the spin-spin interaction may be treated as a small perturbation of the energy levels determined by the large static magnetic field. There will be four eigen states of the pair in the unperturbed system (+ +), (+ −), (− +) and (− −), where the first sign represents the state of the I particle and the second the state of the S particle in the magnetic field. Let the occupational numbers of each of these states be N_{++}, N_{+-}, N_{-+} and N_{--} respectively. The transition probabilities per unit time between these states are shown diagrammatically in figure 2.

The rate of change of the occupational numbers may be obtained from these transition probabilities.

$$\frac{dN_{++}}{dt} = -(\omega_1 + \omega_1' + \omega_2)N_{++} + \omega_1' N_{+-} + \omega_1 N_{-+} + \omega_2 N_{--} + \text{const.}$$

$$\frac{dN_{+-}}{dt} = \omega_1' N_{++} - (\omega_0 + \omega_1 + \omega_1')N_{+-} + \omega_0 N_{-+} + \omega_1 N_{--} + \text{const.}$$

$$\frac{dN_{-+}}{dt} = \omega_1 N_{++} + \omega_0 N_{+-} - (\omega_0 + \omega_1 + \omega_1')N_{-+} + \omega_1' N_{--} + \text{const.}$$

$$\frac{dN_{--}}{dt} = \omega_2 N_{++} + \omega_1 N_{+-} + \omega_1' N_{-+} - (\omega_1 + \omega_1' + \omega_2)N_{--} + \text{const.}$$

... 1.5.1.

The constants may be obtained by considering the system in thermal equilibrium.

The macroscopic magnetic moments $\bar{I}_z$ and $\bar{S}_z$ are given by :

$$(N_{++} + N_{+-}) - (N_{-+} + N_{--}) = K\bar{I}_z$$

$$(N_{++} + N_{-+}) - (N_{+-} + N_{--}) = K\bar{S}_z$$

... 1.5.2.

Inserting the values of 1.5.2 in 1.5.1. and computing the rate of change of the macroscopic magnetic moment of $\bar{I}_z$ one obtains the result :

$$\frac{d\bar{I}_z}{dt} = -(\omega_0 + 2\omega_1 + \omega_2)(\bar{I}_z - I_0) - (\omega_2 - \omega_0)(\bar{S}_z - S_0)$$

... 1.5.3.

I_0 and S_0 are the equilibrium values of the macroscopic magnetic moments which take into account the constants of equation 1.5.1.

In equilibrium the rate of change of $\bar{I}_z$ is zero and $\bar{I}_z$ may be written :

$$\bar{I}_z = I_0 + \frac{\omega_2 - \omega_0}{\omega_0 + 2\omega_1 + \omega_2}\left(S_0 - \bar{S}_z\right) \qquad \dots\ 1.5.4.$$

If an intense radiation field is applied to the specimen at the resonance frequency of the spins S the states $S=+\frac{1}{2}$ and $S=-\frac{1}{2}$ will be equalised in population and $\bar{S}_z = 0$. $\bar{I}_z$ now becomes :

$$\bar{I}_z = I_0 + \frac{\omega_2 - \omega_0}{\omega_0 + 2\omega_1 + \omega_2} S_0 \qquad \dots\ 1.5.5.$$

In order to evaluate the Overhauser effect in this case it is necessary to compute the transition probabilities which occur in 1.5.4.

<u>Calculation of Transition Probabilities.</u>

The transition probability per unit time from the eigen state $|n\rangle$ to the eigen-state $|n'\rangle$ may be obtained from first order perturbation theory (Dirac, 1935).

$$\omega_{ij} = \frac{1}{\hbar^2}\left| \int_0^t \langle n'|\mathcal{H}(t)|n\rangle e^{-i2\pi\nu_{ij}t'} dt' \right|^2 \qquad \dots\ 1.5.6,$$

where

$$\nu_{ij} = \frac{(E_{N'} - E_{N})}{h} \qquad \text{... 1.5.7.}$$

The heat motion of the lattice causes the angles θ and ϕ of 1.4.10 to vary with time. This random motion may be described in terms of a correlation time τ_c defined as :

$$\langle \mathcal{H}(t) \rangle \langle \mathcal{H}^{*}(t+\tau) \rangle = \langle \overline{|\mathcal{H}(0)|}^{2} \rangle e^{-\frac{|\tau|}{\tau_c}} \qquad \text{... 1.5.8}$$

This time-dependent perturbation of the Hamiltonian may now be inserted in 1.5.6 and the integration may be performed. One obtains the following transition probabilities :

$$\omega_0 = \frac{\tau_c}{10 k^2} \; \frac{1}{1 + 4\pi^2 (\nu_I - \nu_S)^2 \tau_c^2}$$

$$\omega_1 = \frac{3 \tau_c}{20 k^2} \; \frac{1}{1 + 4\pi^2 \nu_I^2 \tau_c^2}$$

$$\omega_2 = \frac{6 \tau_c}{10 k^2} \; \frac{1}{1 + 4\pi^2 (\nu_I + \nu_S)^2 \tau_c^2} \qquad \text{... 1.5.9.}$$

These values of the transition probabilities may be inserted in 1.5.5 in order to evaluate the magnitude of the spin polarisation.

A number of interesting cases will be considered.

1.6 Paramagnetic Solutions

In liquids of low viscosity the

correlation time is very short. It is of the order of 10^{-10} second. In this case the transition probabilities of 1.5.9 may be simplified by noting that the denominator becomes practically unity in each case.

$$\bar{I}_z = I_o + 0.5\, S_o \qquad \ldots\ 1.6.1.$$

Writing this in the same form as 1.4.8. one obtains :

$$\frac{M_+}{M_-} = \exp\left[\frac{2\,H(\mu_I + 0.5\,\mu_e)}{kT}\right] \qquad \ldots\ 1.6.2.$$

In this case the spin polarisation is about $\frac{1}{2}$ of the value obtainable in metals and of the opposite sign.

1.7 Diamagnetic Solids with Paramagnetic Impurities.

At low temperatures the molecular correlation time τ_c will be very long. The transition probabilities again can be simplified. Noting that $\nu_s \gg \nu_I$ one obtains :

$$\bar{I}_z = I_o + \frac{5}{7 + 3\left(\frac{\nu_s}{\nu_I}\right)^2} S_o \qquad \ldots\ 1.7.1.$$

In this case a negligible increase in the nuclear spin polarisation occurs.

1.8 Nucleus of a Paramagnetic Ion.

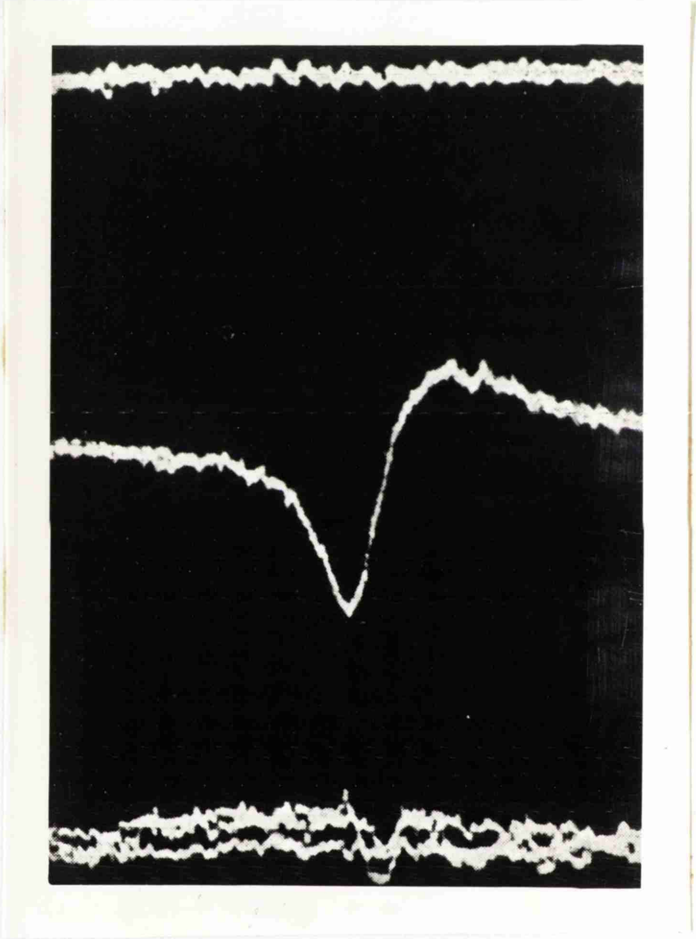


Figure 3

Upper Trace: Lithium Signal lost in Noise

Middle Trace: Overhauser Effect.

Lower Trace: Proton Calibration Signal.

In this case the interaction of the nucleus with the electron is formally the same as that of 1.4.1. Transitions of the type ω_2 and ω_2 do not occur and one obtains :

$$\bar{I}_z = I_0 - S_0 \qquad \ldots 1.8.1.$$

The polarisation in this case is the same as that which is obtained in a metal.

1.9. Experiments on the Overhauser Effect

Shortly after Overhauser's original paper, Carver and Slichter strikingly confirmed his predictions. (Carver and Slichter,1953). Finely divided metallic lithium was subjected to a strong radio-frequency field at 84 Mcs/s in a magnetic field of 30 gauss. With the power available to them they were able to saturate almost completely the electron spin resonance at this frequency. A radio-frequency spectrometer was used to detect the nuclear magnetic resonance absorption of the lithium nuclei. This absorption signal will be proportional to the degree of nuclear polarisation. Approximately a hundred-fold increase in the signal was obtained when the electron resonance was saturated. Figure 3 shows the signal obtained in each case. In the first case the lithium signal is completely lost in "noise".

This experiment was carried out at room temperature and at a very low magnetic field strength. The results obtained showed clearly that Overhauser's predictions were at least approximately correct. The enhancement differed by a factor of about ten from the predicted value. This was attributed to some other relaxation process by which the nuclei were able to relax without coupling to the spin of the conduction electrons.

Soon after this a similar experiment was carried out in a magnetic field of 3300 gauss by Beljers, van der Klint and van Wieringen (1954). In this experiment a 70 watt klystron provided the power to saturate the electron resonance. They used a non-metal, the organic free radical diphenylpicrylhydrazyl. The free electron has a wavefunction which is spread out over much of the molecule. This embraces many of the protons in the two phenyl groups. The nuclear resonance of the protons was detected with a simple marginal oscillator. With the electron resonance partially saturated an enhancement by a factor of 15 was found for the proton polarisation.

It should be noted that in this case the interaction is of the scalar type, $\bar{I}.\bar{S}$, rather than of the dipole-dipole type, because the wavefunction of the electron is finite at the nucleus. Due to the difference in the sign of the magnetic moments of the proton and the electron, I_0 is positive and S_0 is negative, so that, as seen from 1.8.1, $\bar{I}_z$ cannot be negative. The experimental results agreed with this, giving a steady increase of the proton polarisation with increasing electron saturation. If the interaction had been of the dipole-dipole type the proton polarisation would have decreased through zero and then increased in the opposite direction with increasing electron saturation.

Solomon (1955) has reported an experiment of the Overhauser effect on liquid HF at room temperature. In this experiment the two interacting particles were the proton and the ^{19}F nucleus in the HF molecule. The proton resonance was observed while the ^{19}F resonance was subjected to a saturating radio-frequency field. An increase of about 30%

was observed in the proton signal. This is in approximate agreement with the increase of 47% to be expected in a liquid of low viscosity.

1.10 Conclusion

In all the experiments which have been reported the general features of the theory have been verified. However, in all of them the degree of enhancement has fallen short of the theoretical predictions. In each case this has been attributed to the existence of some relaxation process by which the nuclei could relax without interacting with the other spin. If this technique is ever to be used to obtain a target of polarised nuclei it would be important to obtain the full theoretical enhancement. Consequently, it was felt that it would be worthwhile to carry out a theoretical examination of the effect where it would be possible to calculate exactly all the relaxation processes, and then to compare the theoretical predictions with experiment. If agreement was forthcoming then one could predict with some confidence the conditions which would have to be satisfied in order to obtain the maximum nuclear polarisation. The main failure of the published theoretical treatments lie in the fact that only the interaction of the nucleus with a single other particle has been considered. In most solids this is not justified. At temperatures near $1^{\circ}K$ only helium remains a liquid. It was felt essential then to attempt to develop a theoretical treatment of the problem which would be valid in the solid state and in a lattice where the nucleus was able to interact with many particles.

PART II

The Overhauser Effect in Solids. Theory

2.1. Introduction

It was decided to carry out a generalisation of the theory developed by Solomon (1955) on the relaxation processes in a system of two spins. Instead of a single pair of interacting spins, a system of any number of particles of two types will be considered. It will be supposed that these particles are imbedded in a molecular environment which remains in thermal equilibrium at a temperature T °K. The treatment will be carried only so far as to consider the macroscopic magnetic moment of one type of particle when the other is subjected to a strong radiation field. The resulting Overhauser effect will be shown to depend upon the details of the spin-spin and the spin-lattice interactions. In order to carry out the generalisation the treatment will follow to some extent the terminology and methods used by Bloch (1955) in deriving the general Boltzmann equation of a system of nuclear spins.

2.2 The Hamiltonian

A system consisting of two types of particle

I and S is considered. These are imbedded in a lattice which acts as a thermal reservoir at a constant temperature T ^{o}K. The particles possess both spin and magnetic moment. One wishes to compute the macroscopic magnetic moment $\bar{\mu}_I$ due to the particles of spin I when the system is in thermal equilibrium in a constant magnetic field H_0 along the z-direction and also when it has reached a steady state in the presence of a radiation field which reduces $\bar{\mu}_s$ to zero.

The Hamiltonian of the whole system may be written as :

$$\mathcal{H} = E + F + G \qquad \ldots 2.2.1$$

where E represents the Zeeman energy of all the spins in the magnetic field, F represents the energy of the lattice, and G the coupling energy of the spins among themselves and with the lattice. This last term ,G, is considered a small perturbation of the energies of the terms E and F. Without this perturbation the eigenstates of the whole system may be described in terms of an eigen-ket of the form $|ms,jt,fu\rangle$. m refers to the total z-component of the spin of the I particles. In general this value of m will be highly degenerate. The letter s will distinguish between the many possible arrangements of the individual spins which give a particular value of m. Similarly, j will be the total z-component of the spin of the S particles and t the particular arrangement of the individual spins. The energy of the lattice will be given by f and the particular manner in which it is made up by u.

The state of the whole system may be described in terms of the density matrix $\rho_{NN'}$ whose elements are defined as :

$$\rho_{NN'} = \langle ms, jt, fu / \rho / m's', j't', f'u' \rangle$$

In following the behaviour of quantities which depend only upon the values of m and s one may use the distribution matrix $|\sigma|$ whose elements are :

$$\langle ms / \sigma / m's' \rangle = \sum_{fu}{}' \sum_{jt}{}' |\rho| \; \delta_{fu,f'u'} \cdot \delta_{jt,j't'} \qquad \ldots 2.2.2.$$

When the system has reached equilibrium the off-diagonal elements of the density matrix will be zero (Tolman, 1938). One may then write the rate of change of ρ for small changes of ρ as :

$$\frac{d\rho_{NN}}{dt} = \sum_{N'}{}' \left(\rho_{N'N'} W_{N'N} - \rho_{NN} W_{NN'}\right)$$

... 2.2.3,

where $W_{NN'}$ is defined as the transition probability per unit time from the state $|n\rangle$ to the state $|n'\rangle$. By using first order perturbation theory one obtains the following expression for $W_{NN'}$.

$$W_{NN'} = \frac{1}{t\hbar^2} \left| \int_0^t \langle n' | G(t) | n \rangle \, e^{\frac{-i(E_{N'} - E_N)t'}{\hbar}} . dt' \right|^2$$

... 2.2.4

The rate of change of the distribution matrix σ is obtained from equations 2.2.2. and 2.2.3.

$$\frac{d}{dt}\langle ms|\sigma|ms\rangle = \sum_{jt}{}' \sum_{fu}{}' \sum_{n'}{}' \left(\rho_{N'N'} . W_{N'N} - \rho_{NN} W_{NN'}\right)$$

... 2.2.5.

$$\frac{d}{dt}\langle ms|\sigma|ms\rangle = \sum_{fu}{}' \sum_{jt}{}' \sum_{j't'}{}' \sum_{f'u'}{}' \sum_{m's'}{}' \Big\{ \langle m's', j't', f'u' | \rho | m's', j't', f'u' \rangle W_{N'N}$$

$$- \; W_{NN'} \langle ms, jt, fu | \rho | ms, jt, fu \rangle \Big\}.$$

... 2.2.6

In order to complete the summation it is necessary to expand the perturbation, G, in the

Hamiltonian. One may write it in the form :

$$G = \sum_{lk} I_l^{\tau} F_{lk}^{\tau\nu} S_k^{\nu} + \sum_{ll'}' I_l^{\tau} F_{ll'}^{\tau\tau'} I_{l'}^{\tau'} + \sum_{kk'}' S_k^{\nu} F_{kk'}^{\nu\nu'} S_{k'}^{\nu'} + \sum_{lg} I_l^{\tau} F_{lg}^{\tau\alpha} J_g^{\alpha} + \sum_{kg} S_k^{\nu} F_{kg}^{\nu\alpha} J_g^{\alpha} \quad \ldots 2.2.7,$$

where the subscripts 1,k and g refer to the 1th I particle, kth S particle and gth J particle,.etc. The first term of the expansion represents the coupling energy between each of the I particles and each of the S particles. The second term is the coupling energy between like spins in the group of I particles. The third term is that between like members of the group of S particles. The last two terms represent the coupling of the I and S particles directly to the lattice. The coupling to the lattice has been written as if it goes via some particle J_g which possesses both spin and magnetic moment. This is a convenient form to write it for in most cases of interest this is the only way a spin system is directly coupled to the molecular lattice. e.g. If S is a nuclear spin then J_g is the spin of any paramagnetic impurity in the lattice. (Bloembergen, 1949). J in this case may also be another nuclear spin which is coupled to the lattice by its quadrupole moment. If S is an electron spin it may be coupled to the lattice by the spin-orbit interaction. J_g will now represent, not a particle J_g, but the orbital angular momentum of the g^{th} atom.

The operator I_l^τ must obey the following matrix equation :

$$\langle m\ s \,|\, I_l^\tau \,|\, m' s' \rangle = I^\tau_{lm}\ \delta_{m, m'+\tau}\ \delta_{s, s_{l\tau}} \qquad \ldots\ 2.2.8,$$

where the arrangement $s_{l\tau}$ is the same arrangement s' except that the 1-th particle of spin I has changed its component of angular momentum along the z-direction by an amount τ. I^τ_{lm} is the matrix element for the transition in which the z-component of I changes from $I_{m'}$ to $I_{m'+\tau}$. This depends upon the initial m-state of I but not upon the state of the rest of the spins.

Similarly, the operator S_k^ν must satisfy the relation :

$$\langle j t \,|\, S_k^\nu \,|\, j' t' \rangle = S^\nu_{kj}\ \delta_{j, j'+\nu} \cdot \delta_{t, t'_{k\nu}} \qquad \ldots\ 2.2.9,$$

where the arrangement $t'_{k\nu}$ is the same arrangement t' except that the k^{th} particle of spin S has changed its component of angular momentum by an amount ν. A Similar condition must be satisfied by the operator J_j^{α} .

F_{lk} is an operator which acts only upon the variables of the molecular environment associated with the particles specified in the subscript. e.g. $F_{lk}^{00} = \frac{\hbar^2 \gamma_I \gamma_S}{r_{lk}^3}(1 - 3\cos^2\theta_{lk})$ (see p. 41.)

In order to simplify the treatment both particles I and S will be assumed to have a spin of ½. The values of τ and ν are then limited to ± 1 and 0. Certain properties of the $W_{NN'}$ may now be noted. Owing to the conditions imposed by equations 2.2.8 and 2.2.9 $W_{NN'}$ does not depend upon the specific values of m and j but only upon the difference τ and ν . Furthermore, since F_{lk} depends only upon the 1th I particle and the kth S particle $W_{NN'}$ does not depend upon the specific value of f but only upon the difference (f - f'). Also, $W_{NN'}$ is symmetric in the initial and final states so $W_{NN'} = W_{N'N}$.

The effect of the perturbation is to remove the degeneracy in both m and j. In the perturbed system each of the arrangements, s and s', will have slightly different energies. Similarly, the different arrangements t and t' will have slightly different energies. These energies will be distributed about the energy determined by m and j respectively in the unperturbed system because G is small compared to either E or F.

It shall be assumed that all the spin I particles considered lie in equivalent positions in the unit cell. Alternatively, if there are two or more non-equivalent sites in the cell, each site may be treated separately and the macroscopic moment for the whole specimen taken as the sum of the magnetic moments of each of the separate sites.

The density matrix can sometimes be written in the simpler form :

$$\langle ms, jt, fu | \rho | ms, jt, fu \rangle = \langle ms | \sigma | ms \rangle \, \Theta(jt) \, \Pi(fu).$$

... 2.2.10,

where $\Pi(f,u)$ may be written explicitly in the form

$$\Pi(fu) = \frac{e^{-\frac{E(fu)}{KT}}}{\sum\limits_{f'u'} e^{-\frac{E(f'u')}{KT}}}$$

T is the temperature of the lattice and E(fu) is the energy of the molecular state $|fu\rangle$.

Similarly, $\Theta(jt)$ may be written explicitly as:

$$\Theta(jt) = \frac{e^{-\frac{E(jt)}{KT_s}}}{\sum\limits_{j't'} e^{-\frac{E(j't')}{KT_s}}}$$

In this expression T_s is a parameter which describes the probability of finding the S-particles in a particularl energy state $|jt\rangle$ of energy E(jt). This form of expression is not generally true but in the two cases considered it is. In the case of thermal equilibrium it is obviously true and, when the spin states are saturated i.e. $T_s = \infty$ it is also true.

Because G is a small perturbation $\langle ms|\sigma|ms\rangle$ will be approximately equal to $\langle ms'|\sigma|ms'\rangle$ $\langle m|\sigma|m\rangle$ will be written as the average value of $\langle ms|\sigma|ms\rangle$ for all arrangements s. Equation 2.2.6 may now be written in the form :

$$\frac{d}{dt}\langle m|\sigma|m\rangle = \sum_{m'}{}' \sum_{jt} \Theta(jt) \sum_{fu} \Pi(fu)\Bigg[\sum_{\Delta E_{jt}} e^{-\frac{(E_{j't'}-E_{jt})}{kT_s}} \times \sum_{ss'}\sum_{\Delta E_{fu}} e^{-\frac{(E_{f'u'}-E_{fu})}{kT}} \langle m'|\sigma|m'\rangle W_{N'N} - \langle m|\sigma|m\rangle \sum_{\Delta E_{jt}} \sum_{\Delta E_{fu}}{}' \sum_{s's} W_{NN'}\Bigg]$$

... 2.2.11.

From the definition of Θ(jt) and Π(fu) one obtains unity for the summation over jt and fu. Replacing m' by m - 1 the ratio $\langle m|\sigma|m\rangle / \langle m-1|\sigma|m-1\rangle$ which in independent of the particular value of m, is obtained: (See Appendix I.)

$$\frac{\langle m|\sigma|m\rangle}{\langle m-1|\sigma|m-1\rangle} = \frac{\sum\limits_{\Delta E_{jt}} e^{-\frac{E_{jt'}-E_{jt}}{\kappa T_s}} \sum\limits_{\Delta E_{fu}} e^{-\frac{E_{fu'}-E_{fu}}{\kappa T}} \sum\limits_{ss'} W_{N'N}}{\sum\limits_{\Delta E_{jt}} \sum\limits_{\Delta E_{fu}} \sum\limits_{ss'} W_{NN'}}$$

$$= e^{-\alpha} \qquad \ldots\ 2.2.12.$$

Hence

$$\langle m|\sigma|m\rangle = A\,e^{-\alpha m} \qquad \ldots\ 2.2.13.$$

A is a constant which may be obtained from the requirement that :

$$\sum_{ms} \langle ms|\sigma|ms\rangle = 1 \qquad \ldots\ 2.2.14.$$

The macroscopic expectation value, Q, of any quantity $\langle ms|Q|m's'\rangle$ is obtained by taking the diagonal sum of the matrix product

$$\langle ms, jt, fu/\rho/m's', j't', f'u'\rangle\langle m's'/Q/m''s''\rangle$$

As Q depends only upon ms for pure spin I quantities it is sufficient to take the trace of the matrix product of $\langle ms/\sigma/m's'\rangle\langle m's'/Q/m''s''\rangle$

Hence

$$\bar{\mu} = \sum_{ms} \langle ms|\sigma|ms\rangle\langle ms|m\gamma_{I}\hbar|ms\rangle$$

$$\ldots\ 2.2.15$$

The many discrete states $|ms\rangle$, $|ms'\rangle$ .... etc., may be replaced by a continuum of states having a density $\eta_m(s).ds$ with the quantum number m and energy lying between s and $s + ds$. $\langle ms|\sigma|ms\rangle$ may now be written as :

$$\langle ms|\sigma|ms\rangle = \langle m|\sigma|m\rangle \cdot \eta_m(s).ds \qquad \ldots\ 2.2.16.$$

To a good approximation

$$\int_s \eta_m(s).ds = g_m \int_s \eta(s).ds \qquad \ldots\ 2.2.17,$$

where g_m is the degeneracy of the particular value of m and $\eta(s)$ is a shape function which does not depend upon m. This approximation is valid provided that the vector $\vec{r}_{lk}$ joining any two particles in the system may have any orientation with respect to the z-direction. The value of g_m is given by the Binomial coefficient $\binom{n}{\frac{n}{2}-m}$ for spin $\frac{1}{2}$ particles, the number of I particles being n .

$\bar{\mu}$ is obtained by putting in the values of $\langle ms|\sigma|ms\rangle$ from equations 2.2.16 and 2.2.13 and fulfilling the requirement of 2.2.14.

$$\bar{\mu} = \frac{\gamma_I \hbar \sum_m m\, g_m e^{-\alpha m}}{\sum_m g_m e^{-\alpha m}} \qquad \ldots\ 2.2.18$$

The summation is carried out by using the binomial expansion yielding the result :

$$\overline{\mu} = -\frac{\hbar \gamma_{in}}{4}\alpha$$

... 2.2.19,

provided that α is small compared to unity (Appendix II.)

2.3. Thermal Equilibrium

In the case of thermal equilibrium T_s becomes equal to the lattice temperature $T\,^{\circ}K$. Furthermore energy must be conserved within the system so that :

$$E(jt) + E(fu) + E(ms) = E(j't') + E(f'u') + E(m's').$$

... 2.3.1

Provided that $\eta(s)$ varies symmetrically about its mean value and $W_{NN'}$ is a slowly varying function of s then from equation 2.2.12, α is given by :

$$\alpha = \frac{\gamma \hbar H_0}{K T}$$

... 2.3.2.

From equation $\overset{(2.2.19.)}{(19)}$ one obtains the value of $\overline{\mu}$ when the system is in thermal equilibrium.

$$\bar{\mu} = -n \frac{\hbar^2 \gamma_I^2 H_0}{4\kappa T}$$

... 2.3.3.

2.4. The Overhauser Effect

On the application of a strong radiation field at a frequency corresponding to transitions in which j changes by ± 1, T_s rises above the temperature T of the lattice. In the limit of a very strong radiation field T_s becomes infinite. In this case equation 2.2.12 can be written :

$$e^{-\alpha} = \frac{\sum_{\Delta j_I} \sum_{\Delta j_u} e^{-\frac{E_{j_u'} - E_{j_u}}{\kappa T}} \sum'_{s's} W_{n'N}}{\sum_{\Delta j_I} \sum_{\Delta j_u} \sum_{s's} W_{nn'}}$$

... 2.4.1.

It is now necessary to consider in detail the transition probabilities $W_{NN'}$ which occur in the summation 2.4.1. In all these transitions the total energy of the system must be conserved because the perturbation, G, is independent of the time. However, when the perturbation is expanded in the form 2.2.7, the individual terms of the expansion become dependent upon the time. In order to calculate the transition probabilities it is necessary to know their explicit time dependence.

The time dependence of each of the operators I, F and S may be specified by the correlation times τ_i, τ_c and τ_s respectively. These are defined in the usual way by :

$$\langle I(t+\tau)\rangle\langle I^*(t)\rangle = \langle\overline{|I(0)|}\rangle^2 e^{-\frac{|\tau|}{\tau_i}} \qquad \ldots\ 2.4.2$$

$$\langle F(t+\tau)\rangle\langle F^*(t)\rangle = \langle\overline{|F(0)|}\rangle^2 e^{-\frac{|\tau|}{\tau_c}} \qquad \ldots\ 2.4.3$$

$$\langle S(t+\tau)\times S^*(t)\rangle = \langle\overline{|S(0)|}\rangle^2 e^{-\frac{|\tau|}{\tau_s}} \qquad \ldots\ 2.4.4.$$

(Andrews, 1955)

It is convenient to group the $W_{NN'}$ which occur in equation 2.4.1 according as the change in j is zero or ± 1. Equation 2.4.1 can be rewritten in the form :

$$e^{-\alpha} = \frac{\sum_{l=-1}^{l=+1} U_l \, e^{-\frac{E_{j'_u} - E_{j_u}}{KT}}}{\sum_{l=-1}^{l=+1} U_l} \qquad \ldots\ 2.4.5,$$

where

$$U_l = \sum_{\Delta E_{j_l}}{}' \; \sum_{\Delta E_{j_u}}{}' \; \sum_{s's}{}' \; W_{N'N} \qquad \ldots\ 2.4.6.$$

Two extreme conditions of the lattice corresponding firstly to a rigid thermal lattice and secondly to a non-rigid lattice will be considered.

2.5 The Rigid Lattice

The rigid lattice will be defined as one in which the correlation time τ_c of equation 2.4.3 shall be long compared to either τ_i or τ_s. In this case on inserting expressions 2.4.2, 2.4.3 and 2.4.4 in 2.2.4 one obtains a negligible contribution to the time dependence of the expression from the molecular correlation time τ_c. Consequently, the transition probabilities in which f changes are small compared to those in which f remains unchanged. Hence, one obtains from 2.4.5

$$\alpha = 0 \qquad \ldots\ 2.5.1.$$

and from expression 2.2.19 :

$$\bar{\mu} = 0 \qquad \ldots\ 2.5.2.$$

2.6. The non-rigid lattice

The non-rigid lattice will be defined as one in which the molecular correlation time τ_c shall be short compared to both the spin correlation times τ_i and τ_s. In this case the time dependent part of 2.2.4 comes from the operator F and the other operators I and S may be removed from under the integral sign. It may then be shown that :

$$W_{NN'} = \sum_{\substack{\ell \cdots K \\ etc.}} \frac{1}{\hbar^2} \left| \overline{I^{\tau}_{\ell m} F^{\tau\nu}_{\ell K} S^{\nu}_{Kj}} \right|^2 \frac{2\tau_c}{1+\omega_j^2\tau_c^2}$$

... 2.6.1,

where $\hbar\omega_j$ is the energy difference between the states $|m-1, s'; j- \ , t'\rangle$ and $|ms, jt\rangle$. From 2.3.1 is also the difference of energy of the states $|f, u\rangle$ and $|f'u'\rangle$.

When the explicit form of the dipole-dipole perturbation is used the operator $F_{\ell K}$ may be written as :

$F^{00}_{\ell K} = c_{\ell K}(1 - 3\cos^2\theta)$;

$F^{-1,1}_{\ell K} = F^{1,-1}_{\ell K} = c_{\ell K}(\frac{1}{2} - \frac{3}{4}\sin^2\theta)$;

$F^{\pm 1,0}_{\ell K} = F^{0,\pm 1}_{\ell K} = -c_{\ell K}\, 3/2 \sin\theta\cos\theta\, e^{\pm i\phi}$;

$F^{\pm 1,\pm 1}_{\ell K} = -\frac{3}{4} c_{\ell K} \sin^2\theta\, e^{\pm 2i\phi}$, where

$c_{\ell K} = \dfrac{\hbar^2 \gamma_I \gamma_S}{r^3_{\ell K}}$ 2.6.2.

The polar angles θ and ϕ have been introduced to characterise the orientation with respect to the z-axis of the vector $\vec{r}_{\ell K}$, which joins the 1st and

k^{th} particles.

The fact that the transition probabilities of 2.6.1 depend through 2.6.2 upon the inverse sixth power of the separation r_{lk} of the interacting particles makes it possible to simplify the summation of 2.2.7 and hence of 2.4.5. In many cases a good approximation is obtained by taking the summation over nearest neighbours only.

In a polycrystalline material a further simplification is provided by the fact that the vector $\vec{r}_{lk}$ joining any pair of particles may have any orientation with respect to the z-axis. The summation over all the particles may then be replaced by a small number of terms, where each term represents the interaction of a pair of neighbouring particles (m,n) in the unit cell averaged over all orientations of the cell. $\overline{|I^{\tau}_{lm} F^{\tau\nu}_{lk} S^{\nu}_{k}|^2}$ may be replaced by the average over all orientations of $\overline{|I^{\tau}_{m} F^{\tau\nu}_{mn} S^{\nu}_{n}|^2}$.

By using the same approximations as were used in obtaining 2.2.19 one can obtain $\bar{\mu}$. This is given by the following expression :

$$\bar{\mu} = -n \frac{\hbar^2 \gamma_I^2 H_0}{4kT} \cdot \frac{\sum_l Y_l \left(1 + l\frac{\gamma_S}{\gamma_I}\right)}{\sum_l Y_l} \qquad \ldots 2.6.3$$

where

$$Y_{l\ l\neq 0} = \frac{1}{\hbar^2}\sum_{MN}\overline{|I^+_m F^{+1,l}_{mn} S^l_n|}^2 \ \frac{2\tau_c}{1+(\omega_I+l\omega_S)^2\tau_c^2}$$

... 2.6.4.

$\frac{\omega_I}{2\pi}$ is the Larmor precession frequency of the I particles in the magnetic field and $\frac{\omega_S}{2\pi}$ that of the S particles.

Y_0 is given by the following expression :

$$Y_0 = \frac{2\tau_c}{\hbar^2}\Big[\frac{1}{1+\omega_I^2\tau_c^2}\Big\{\sum_{MN}\overline{|I^{+1}_m F^{+1,0}_{mn} S^0_n|}^2 + \sum_{mq}\overline{|I^1_m F^{1,0}_{mq} I^0_q|}^2\Big\}$$

$$+\frac{1}{1+4\omega_I^2\tau_c^2}\Big(\sum_{mq}\overline{|I^{+1}_m F^{+1,+1}_{mq} I^{+1}_q|}^2\Big)$$

$$+\sum_{\alpha=-1}^{\alpha=+1}\frac{1}{1+(\omega_I+\alpha\omega_g)^2\tau_c^2}\sum_{mg}\overline{|I^{+1}_m F^{+1,\alpha}_{mg} J^\alpha_g|}^2$$

... 2.6.5

The summations occurring in 2.6.4 and 2.6.5 are simplified by noting that :

$$\overline{|J^\pm|}^2 = \frac{2}{3}J(J+1)(2J+1)$$

$$\overline{|J^0|}^2 = \frac{1}{3}J(J+1)(2J+1)$$

$$\overline{|F^{++}_{lK}|}^2 = \overline{|F^{+,0}_{lK}|}^2 = \frac{3}{10}C^2_{lK}$$

etc. ... 2.6.6

$$\overline{|F^{+,-}_{lK}|}^2 = \frac{1}{20}C^2_{lK}$$

(See Appendix)

In equations 2.6.4 and 2.6.5 the subscripts m and q refer to I particles whereas the subscript n refers to S particles. In 2.2.7 the interaction of the particles I and S with the lattice was written as if the interaction went via some other particle J_q possessing a magnetic moment. $\frac{\omega_q}{2\pi}$ is the Larmor precession frequency of the J particles in the magnetic field.

It is convenient at this point to consider the validity of the result contained in equation 2.6.3.

2.7 Validity of Result

It has been assumed that :

(a) The molecular lattice remains in thermal equilibrium at a temperature T^{o}K.

(b) The motion of the molecular lattice may be described in terms of a single correlation time τ_c .

(c) This molecular correlation time τ_c is short compared to the spin correlation times.

(d) The mean width of a particular m or j energy level is small compared to the respective separation of these levels in the magnetic field.

(e) The separation of these levels in the magnetic field is small compared to kT.

(f) The particles I and S have spin $\frac{1}{2}$.

(g) The material is in powder or polycrystalline form.

(h) The S spin system may be described by a temperature T_s in the presence of the saturating radiation field.

In the case where the particles J_q are nuclei and have spin $\frac{1}{2}$ the assumption (a) may not be justified. The reason for this is that the Overhauser effect may upset the thermal equilibrium distribution of the J particles. If J has a spin greater than $\frac{1}{2}$ the interaction to the lattice via the quadrupole moment of the particle usually will be stronger than the magnetic spin-spin interaction between the particles. In this case the J_j particles remain in thermal equilibrium with the lattice and the assumption (a) is justified.

In the next section the theoretical results obtained in this section will be compared with the results obtained from an experimental investigation of the Overhauser effect.

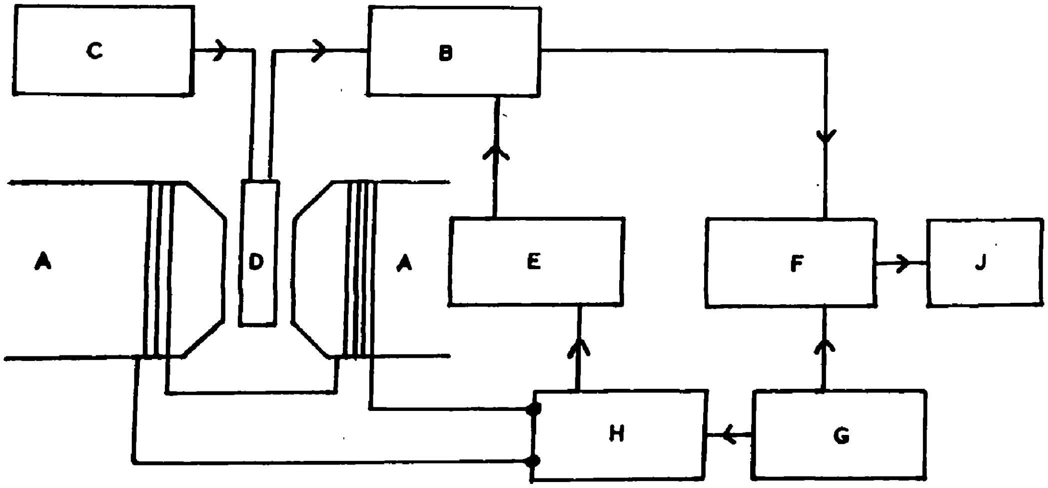


Figure 4

Diagrammatical Sketch of Apparatus.

PART III

APPARATUS

3.1 General Requirements

It was decided to investigate the spin-spin interaction between nuclei of different magnetic moments rather than between the electron and a nucleus. The reason for doing this were as follows. A very large range of compounds is available for which the crystal structures are known. Unlike the electron the position of the nucleus can be very exactly located in the unit cell. The experimental technique is greatly simplified by the fact that large magnetic fields may be used without the need of microwave components.

Figure 4 gives a diagrammatical representation of the apparatus which was used. A are the poles of the magnet in the field of which the experiments were carried out. B is a nuclear magnetic resonance spectrometer for observing the polarisation of the nuclear spin. C is an oscillator which saturates the spin levels of the other set of nuclei. D is a bridge box containing the specimen. In order to obtain greater sensitivity the magnetic field was modulated at 315 c/s about its mean value and a lock-in detector was used. G is the 315 c/s oscillator feeding the power amplifier H, which feeds current to the sweep coils on the magnet and also to a calibrator unit, E, which balances out any signal that is picked up directly from the modulation coils. F is the phase-sensitive detector and J is the pen-recorder. A description of each of these items will be given separately.

3.2. Magnet System

During the course of the investigation three different magnet systems were used. At first the only magnet available was an electromagnet with 2" polepieces and an adjustable gap. This magnet could provide a field of 6000 gauss in a gap of width 1 cm when supplied with a current of 0.7 amps at 110 volts.

Field Homogeneity

It was found impossible to detect the nuclear magnetic resonance of the protons in oil with this magnet because the field in the gap was insufficiently uniform over the volume of the specimen. In order to improve the homogeneity of of the field two pole-pieces of 3" diameter were cut of soft iron. Three brass adjustment screws situated at 120° around the circumference allowed the pole-pieces to be tilted with respect to one another. A homogeneity of about 0.2 gauss over a 1 c.c. volume was obtained with this arrangement. A higher input power to the magnet was required in order to obtain the same magnetic field in the gap.

Stabilised Current Supply

In order to use this magnet it was necessary to design a power supply which could give the required current at a suitable voltage. The design was based on the following considerations. A stability of approximately 1 part in 10,000 was required over a period of about 10 seconds. For reasonable versatility it was decied to have the output current continuously variable over its full range. An unstabilised direct current supply of ample capacity was available from the 250 volt d.c. mains. Superimposed upon the mean d.c. level was a ripple of about 20 volts at 300 c/s.

It was decided to use a circuit in which the magnet current was obtained from the d.c.mains

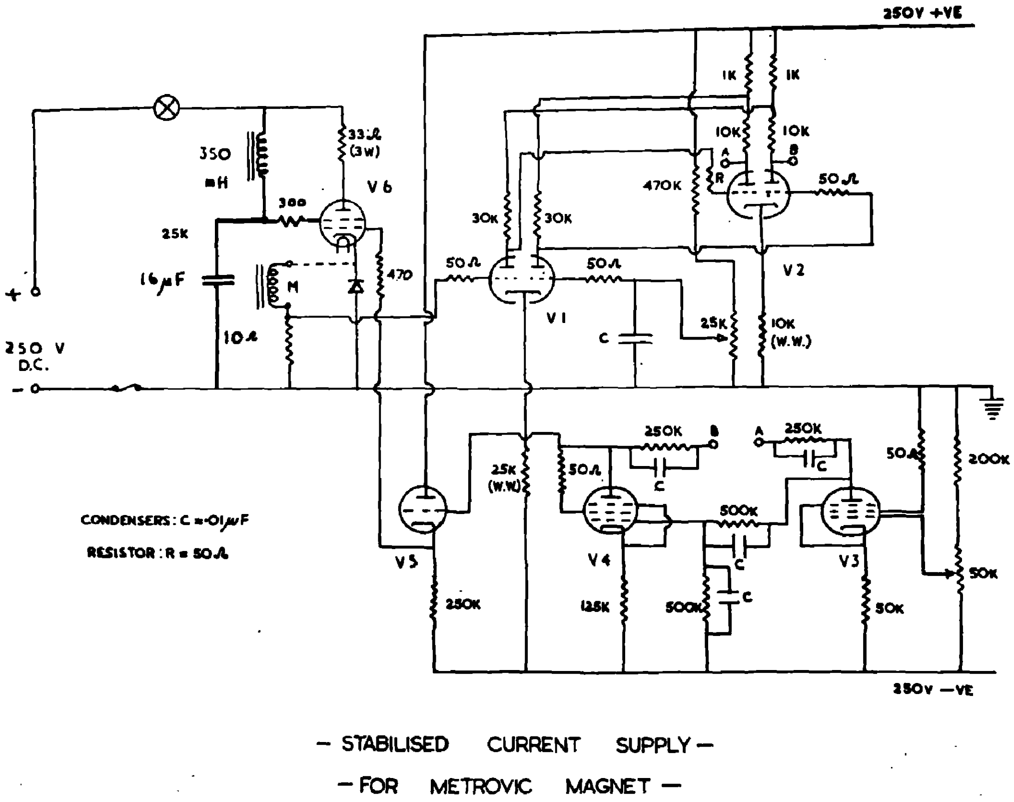


Figure 5

Stabilised Current Supply.

and passed through a number of series control valves strapped in parallel. The grids of the series valves were controlled by the output of a d.c. amplifier which measured the difference between the voltage drop across a standard resistor carrying the magnet current and an adjustable potential.

Figure 5 gives the circuit diagram of the stabilised power supply. Owing to the fact that the circuit incorporates a number of novel features a description of its operation will be given.

The first valve of the difference amplifier, V1 is a double triode with a common cathode. Both grids have the same cathode with the result that slow drifts in the difference of the contact potential between the two grids and the cathode are reduced to about 3 millivolts. (Chance et al, 1949). The anodes of this valve are directly connected to the grids of the next stage. Positive feedback is obtained from the 1 k resistors in the anode loads of V2. The valves V3 and V4 are used to bring the output of the difference-amplifier down to a potential suitable for controlling the grids of the series control valves V6. V3 is a constant current pentode which maintains a constant potential difference across its 250 K anode load. The variations of potential on the anode of V3 are halved by the high-frequency compensated potential divider and fed to the grids of a cathode follower. The anode and cathode loads of this cathode follower are adjusted so that the potential at the anode remains fixed if the potential of A and B move in the same direction. If the potential of A and B move in opposite directions then this point moves the sum of these differences.

The pre-set potentiometer R1 adjusts the current through the constant current pentode V3 and , indirectly, the potential at the anode of V4.

The output is taken from the anode of V4 and fed to a cathode follower V5 which drives the grids of the series valves. In order to reduce the ripple in the magnet current the sreen current to the series valves is smoothed by a choke and condenser filter unit. The effect of this is to increase the anode impedance of the series valves from that of a triode to that of a pentode for rapid fluctuations in the anode voltage.

A metal rectifier was connected across

the magnet as a protective device in the event of a sudden failure in the H.T. supply. Five type CV 345 valves were strapped in parallel in order to obtain the required current. Parasitic stopper resistors were required on each of the grid and screen grid leads.

The reference potential was obtained from a potential divider of standard high stability resistors supplied from 10 type N dry cells. It was noted that a slow drift in current occurred due to the change of the E.M.F. of the cells with room temperature. For satisfactory operation it was found necessary to keep the cells away from the series valves and near an open window. In a later modification the reference potential was obtained from the stabilised H.T. line of the difference amplifier.

The performance of the supply is summarised in the accompanying table.

Table I

Output	0 - 1.5 amps
Ripple	0.30 milliamps.
Stability	0.01% for 5% mains variation.
Long Term Stability	3 parts in 10^4

This magnet and the power supply were used for the first experiments of the Overhauser effect on ammonium fluoride. However, when it was realised that it would be necessary to house the specimen in a cryostat in order to take measurements at various temperatures, this magnet was found to be inadequate. The magnet gap was too narrow to allow access of a suitable cryostat. At this time another magnet became available for this work. This magnet had pole-pieces 4" in diameter, and a field of 7000 gauss could be obtained with an input of 9 amps at 60 volts.

Owing to the satisfactory service given by the first power supply it was decided to build a second of similar design. In order to supply the much larger current, 40 type CV345 valves were strapped together. All the filaments were tied in series and connected across the d.c.mains. An 85 ohm resistor could be connected in series with the heaters to enable an initial warm-up to take place before applying the full potential across the filaments.

Considerable trouble was had with dangerous parasitic oscillations building up in the bank of series valves. This was eventually cured by discarding all wire-wound stopper resistors and increasing the grid and screen grid stopper resistors.

This power supply has given satisfactory service. The current stability is similar to that obtained with the smaller power supply.

The uniformity of the field in the gap was improved by mounting two adjustable soft iron shims on the periphery of the pole-pieces. With the shims protruding about 1/10 of an inch into the gap the maximum uniformity was obtained.

This magnet was used for searching for weak resonance in solids. However, most of the final measurements were carried out in the field of a permanent magnet which was obtained just after the large power supply was completed. This permanent magnet provided a field of 3600 gauss between polepieces 4" in diameter and 1.32" apart. Because of a fault in manufacture it was necessary to shim the field in order to obtain a uniformity of 0.2 gauss over a 3 c.c. volume.

3.3. Radio-frequency Spectrometer.

It was decided to use a spectrometer of

the marginal-oscillator type described by Pound (1952) rather than a radio-frequency bridge. The reason for doing this was that the magnetic field and the saturating oscillator could be fixed and the nuclear absorption detected by scanning in frequency. The marginal oscillator has only one tuned circuit so it may be used over a wide range of frequencies with only minor changes to the circuit constants. A bridge on the other hand requires the adjustment of a number of controls in order to balance it at a different frequency.

A great deal of trouble was had with electrical interference in the building. This was minimised by shielding the spectrometer chassis, sanding all coaxial plugs and sockets, decoupling all H.T. and filament leads to the spectrometer with radio-frequency filters and, finally, connecting various parts of the apparatus to earth via suitably placed crocodile clips.

With a spectrometer of this type the sensitivity and the overall noise-figure changes rapidly with increasing r.f. level in the tank circuit. The sensitivity and the r.m.s. noise are plotted together against the r.f. level in

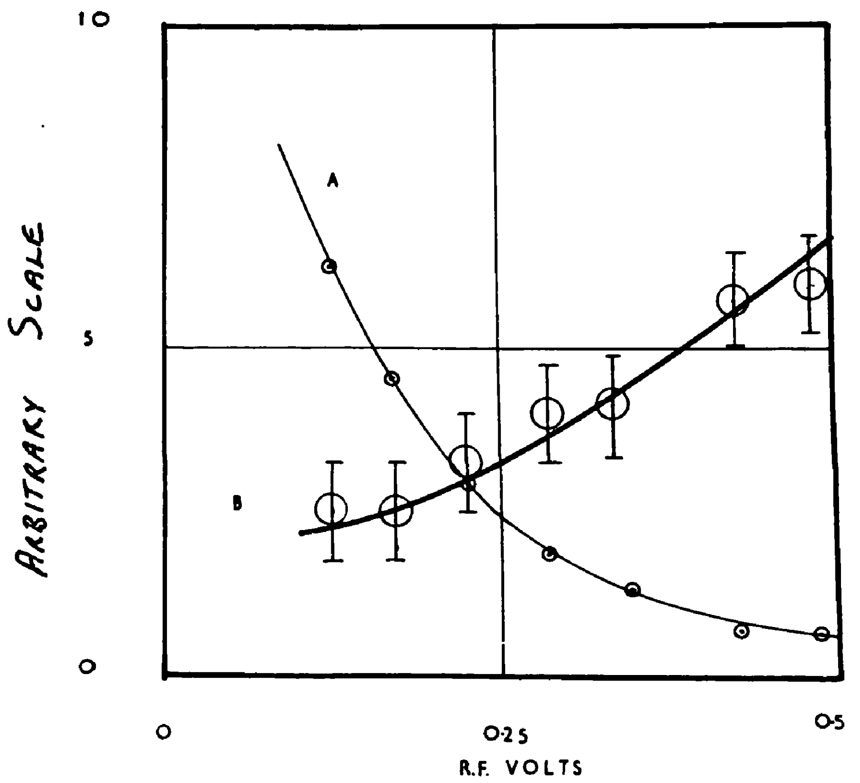


Figure 6

A Detector Sensitivity

B R.m.s. Noise.

figure 6.

Several trivial adjustments were made in the circuit values in order to obtain an improvement in the noise-figure at the various operating frequencies. The oscillator valve was selected from a number of new valves by choosing one which gave the least trouble from microphonics. A crystal detector was incorporated in the circuit in order to monitor the r.f.level in the tank circuit. All the heaters for the spectrometer were supplied from an accumulator. The charging current to the accumulator was adjusted to equal the current drain. In this way the spectrometer gave a very stable performance over long periods of time. Some typical results taken with this spectrometer will be given in section 3.12.

3.4. Field Modulation

An audio oscillator of the type described by Terman (1943a) was built. This gave a pure sine wave output which was stabilised in amplitude and frequency. The output of the oscillator was fed via an adjustable attenuator to a circuit where the phase could be varied over 180°. The output of this circuit fed a power amplifier and an output transformer. This transformer supplied the sweep

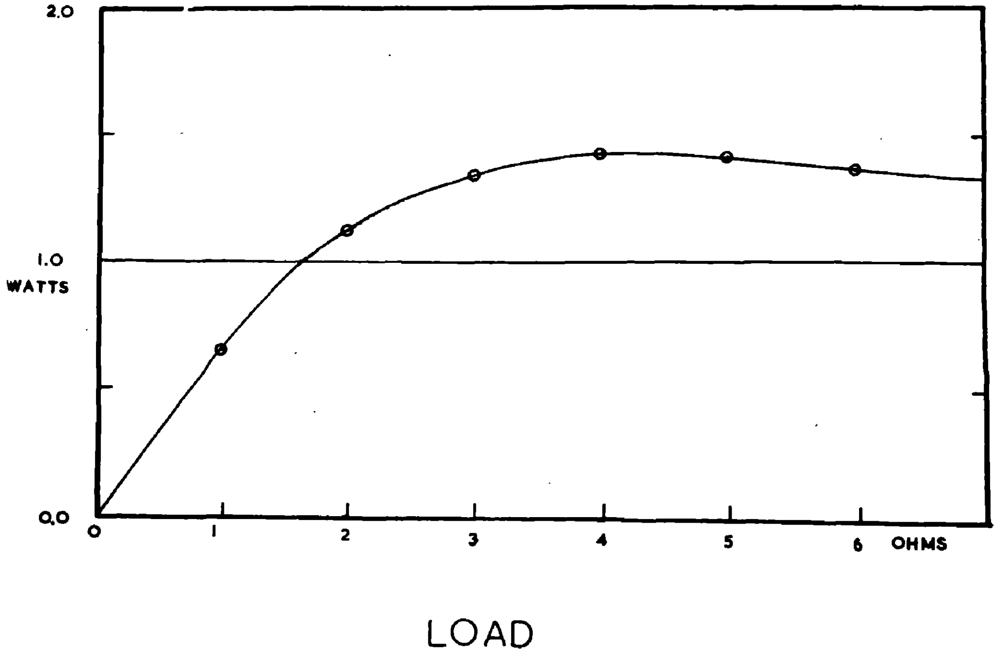


Figure 7

Power Delivered to Load of Power Amplifier.

current to the sweep coils at a low impedance. Figure 7 illustrates the measured output power delivered to loads of different impedance.

A second pair of sweep coils were wound on the magnet so that the magnetic field could be modulated at 50 c/s from the mains. This was useful for checking the field uniformity and for locating strong resonances where the output could be directly displayed on an oscilloscope.

3.5 Phase-sensitive Detector

The output was fed from the spectrometer to a tuned audio-amplifier (Terman,1943b). This comprised a high gain ring-of-three amplifier with negative feedback via a cathode follower and a degenerative network. The degenerative network attenuates the negative feedback at the "resonant" frequency. At this frequency the full gain of the amplifier is obtained. The frequency response of the amplifier is given in figure 8. A gain of approximately 500 was realised at 315 c/s.

The output of this amplifier was fed to the signal input of the phase-sensitive detector. This detector was built according to the specifications

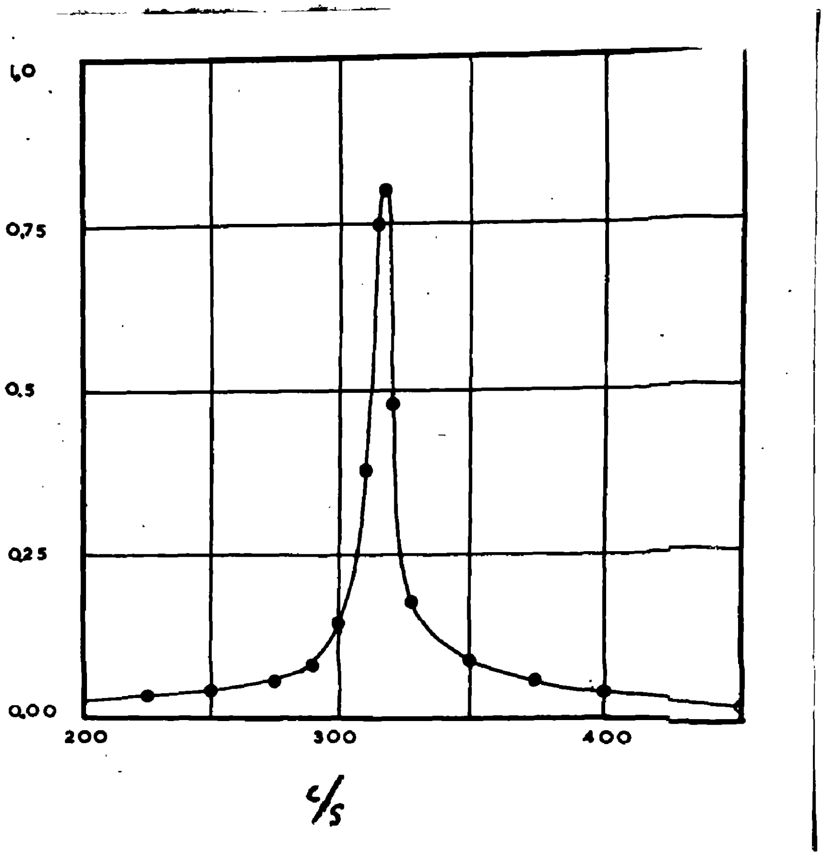


Figure 8

Response of Tuned Audio Amplifier.

of N.Schuster (1951). The reference potential to this detector was obtained from the output of the 315 c/s oscillator. The output of the phase-sensitive detector was fed through a RC filter to a difference amplifier. A 1-0-1 milliameter in the anode circuit of this amplifier displayed the signal. A switch allowed the time constant of the RC filter unit to be varied from 0.1 sec to 30 seconds. A pen-recorder could be connected across this milliameter in order to obtain a permanent trace of a signal.

3.6 Calibrator Unit

A calibrator unit of the type described by Pound (1952) was fed from the output of an attenuator and phase-shifter. The input current to this was obtained from the field modulation power amplifier. This allowed a signal of variable amplitude and phase to be fed into the spectrometer to balance out any 315 c/s signal picked up directly from the modulation coils.

3.7 Power Supplies

All the units were supplied with power from electronically stabilised power supplies. In addition, the power supply for the phase-sensitive detector

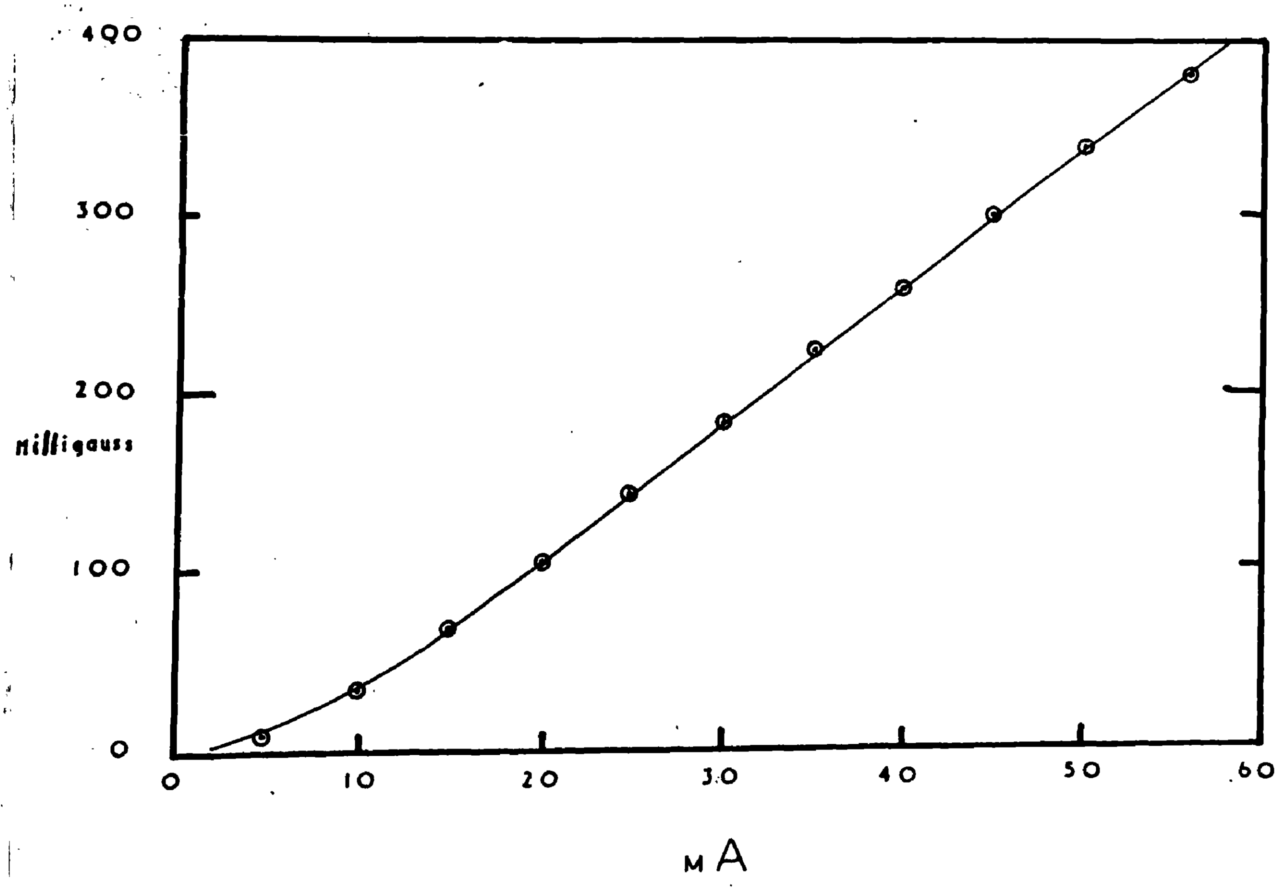


Figure 9

Calibration of Radiofrequency Magnetic Field at the specimen.

was supplied from a voltage stabilised transformer.

3.8 Variable Frequency Oscillator

A 2 watt Hartley oscillator was built using a type CV2127 beam tetrode. A potentiometer across the H.T. supply allowed the screen potential to be varied from 0 to 250 volts. The amplitude of oscillation was controlled by varying this potentiometer. The output was obtained from a link coupling on the tank coil. It was fed via a 70 ohm cable to the bridge box. The amplitude of the radio-frequency magnetic field at the specimen was measured using a crystal diode and a pick-up coil of known cross-sectional area. In figure 9 the r.f. magnetic field is plotted against the input current to the oscillator. This input current is determined by the setting of the screen-grid potentiometer. This approximate calibration was used in order to obtain some idea of the r.f.field at the specimen.

3.9 Radio-frequency Bridge.

In the early experiments of the Overhauser effect on ammonium fluoride a very simple bridge was used. The spectrometer coil and the saturating

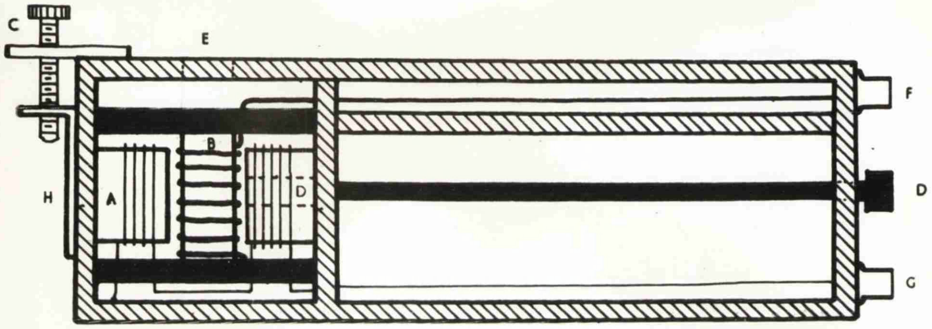


Figure 10

A	Moveable Transmitter Coil
B	Spectrometer Coil
C	V-mode Balance
D	U-mode Balance
E	Hole for Specimen
F	Spectrometer Connection
G	Transmetter Connection.

oscillator coil were mounted orthogonally on a paxolin board. The coils of the saturating oscillator were approximately Helmholtz in design. By varying the position of one of these coils it was possible to decouple the oscillator and spectrometer. Further decoupling was provided by incorporating a band-pass tuned stage in the radio-frequency amplifier of the spectrometer. Both sets of coils were self-supporting. A hole was drilled in the paxolin behind the spectrometer coil so as to avoid any spurious signal from the protons in the paxolin.

A more elaborate bridge was required for work at low temperature. The final arrangement was based on a design by Weaver (1953). A drawing of the essential features of the bridge is given in figure 10. The main body of the bridge was made of $\frac{1}{4}$" brass to ensure adequate rigidity and a large heat capacity. Three different spectrometer coils could be used with the bridge. A coil former of polytetrafluoroethylene (Fluon) was used for all the experiments in which the proton resonance was observed. For the experiments on the ^{19}F and ^{31}P resonances a coil former of paxolin was used.

The transmitter coil was in the form of

a pair of Helmholtz coils on either side of the spectrometer. One of the pair was screwed to a moveable base attached to a differential screw. This screw set the v-mode balance. U-mode balance was obtained by varying the orientation of an inductive loop containing a resistive element (Weaver, 1953). This was mounted on the axis of the stationary transmitter coil near the spectrometer coil.

Two pancake coils were cemented on to the side panels of the box. These provided the field modulation at the specimen.

Connection to the transmitter and spectrometer coils was made by 70 ohm cable and Belling Lee connectors.

With this bridge it was found possible to reduce the voltage pickup from the transmitter coil to less than 2 millivolts with full power delivered to the transmitter coil. The balance point varied slightly with frequency and also with the temperature of the bridge. The bridge was carefully re-balanced before each reading was taken. by noting the r.f. pick-up at the input to the spectrometer. With this bridge it was found possible to dispense with the tuned stage in the r.f. amplifier of the spectrometer.

3.10 Temperature Control

The whole brass box was lagged with $\frac{1}{2}$" of cotton wool. This was then covered by an outer case of cardboard. For measurements above room-temperature a heater element could be screwed in to the main body of the bridge. The heater element was insulated with glass tape. It was wound on a brass rod on No.30 S.W.G. nickel-chrome wire and had a total resistance of 44 ohms. An input of about 100 watts was sufficient to keep the bridge box at 90°C. The heater current was obtained from a variable transformer. This was the highest temperature that could be used because above this the coil supports and wire insulation softened. The box took about fifteen minutes to reach thermal equilibrium at each temperature.

For temperatures below room temperature the heater was replaced by a liquid-air container. The liquid air was kept in a cylindrical copper cup 4" high and 2" in diameter which was heavily lagged with cotton wool and glass tape. An 0 B.A. screwed

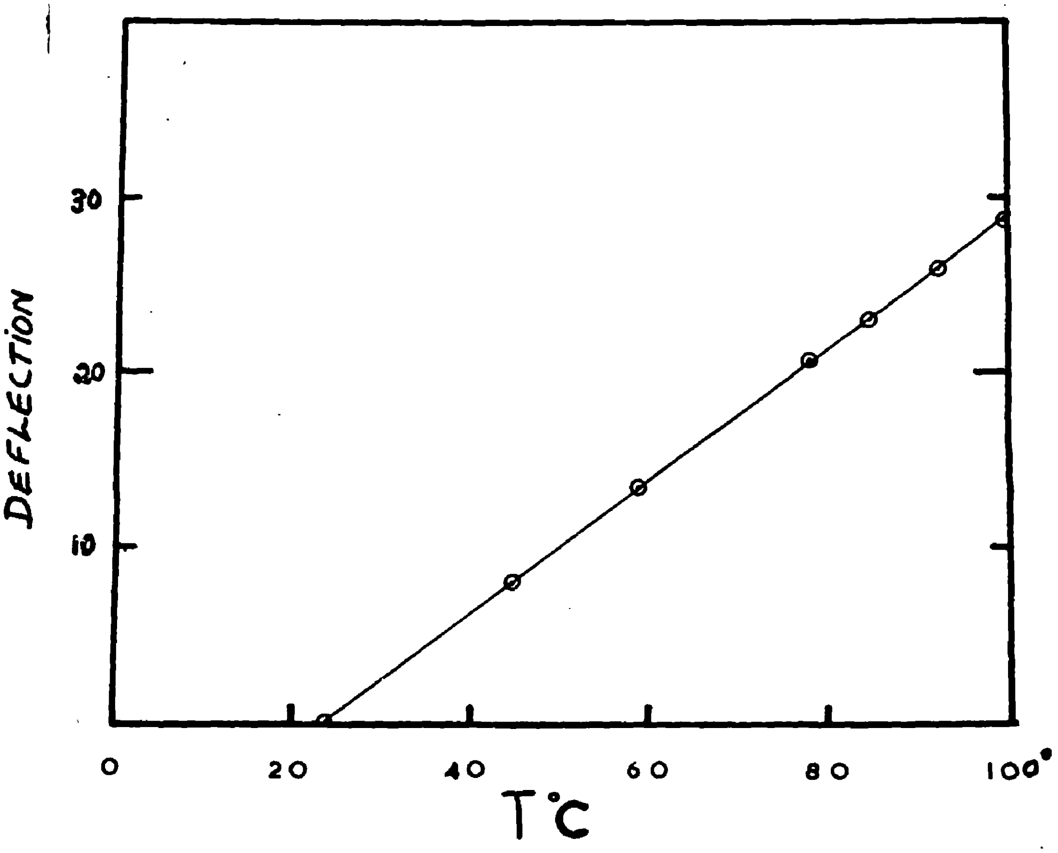


Figure 11

Thermocouple Calibration

brass rod was soldered to the base of this cup. The temperature of the bridge would be varied over the range from $+5^{\circ}$C to -80°C by varying the length of the rod between the cup and the body of the bridge.

A copper-constantan thermocouple was mounted in the bridge box next to the spectrometer coil. A spot-galvanometer was used to monitor the temperature of the specimen. The thermocouple calibration is given in figure 11.

3.11 Accessories

In order to make it possible to record automatically the nuclear magnetic resonance absorption signals and to reduce the labour of searching for weak signals, a motor-driven tuning condenser was constructed. A shaded-pole motor drove a 1024 to 1 reduction gear which turned the rotor shaft of a small variable condenser. Different pulleys could be used between the motor and the reduction gear in order to get a suitable sweep rate. A second motor and gearbox was built to provide a slow sweep for the main current to the large electromagnet.

The tuning dial of a communications

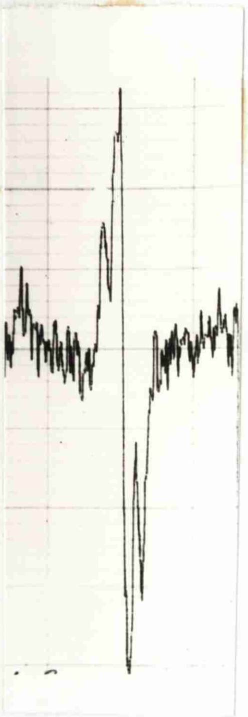
receiver was accurately calibrated at 100 Kcs/sec points by using a crystal oscillator and a signal generator. The frequencies at which the nuclear resonance of ^{1}H, ^{2}H, ^{7}Li, ^{11}B, ^{19}F, ^{23}Na, ^{31}P, ^{79}Br and ^{81}Br occurred in the field of the permanent magnet were logged on this dial.

3.12 Preliminary Experiments

A number of preliminary experiments were carried out in order to check the behaviour of the apparatus and to gain experience in operating it. As noted above, the nuclear resonance frequencies of a number of isotopes were determined in the field of the permanent magnet. The proton and deuterium resonances were detected in water and heavy water respectively. The ^{7}Li resonance was observed in an aqueous solution of LiCl. The resonances of ^{11}B, ^{19}F, ^{23}Na, ^{31}P, and the bromine isotopes were observed in aqueous solutions of their salts using the phase-sensitive detector.

The proton resonance was observed in a number of solids. An interesting result was obtained from a single crystal of naphthalene.

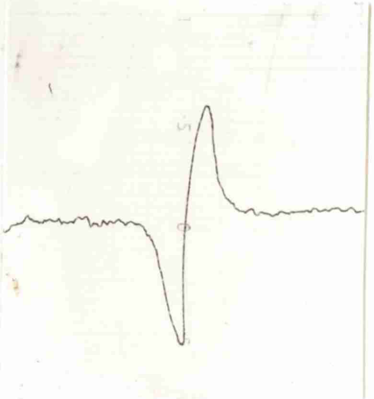
A single crystal of naphthalene was mounted



Trace 1

Naphthalene Crystal

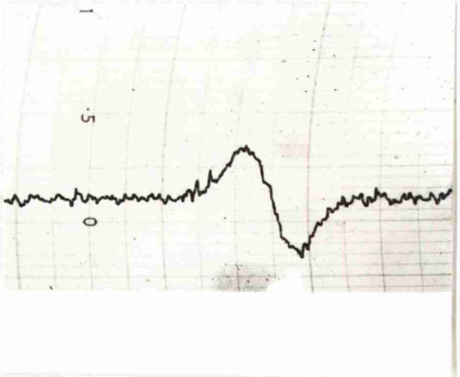
Proton Resonance



Trace 2

Proton Resonance

Ammonium Fluoride



Trace 3

Phosphorus Resonance in Phosphonium Iodide.

in the spectrometer coil with the cleavage plane perpendicular to the direction of the magnetic field. The phase-sensitive detector was used and the field modulation was set at a value less than the magnetic line width. The recorded trace (Trace 1) represents the first derivative with respect to the magnetic field of the nuclear absorption. Figure 12 is the result obtained from carrying out a point by point integration of this curve.

The result is readily explained as a triplet in which the centre line has twice the statistical weight of the two satelites. This is what one should expect for naphthalene. The crystal cleaves in a plane approximately parallel to the plane of the molecule. Thus each proton in the molecule has two neighbouring protons lying at an angle of 90° to the direction of the magnetic field. The local field at the proton due to the magnetic moment of these neighbours can thus have one of three values. Both neighbours may be in the $+\frac{1}{2}$ state, both neighbours may be in the $-\frac{1}{2}$ state or one may be in the $+\frac{1}{2}$ and the other in the $-\frac{1}{2}$ state. This last situation may be obtained in two different ways and hence it has a statistical weight of two. The field of

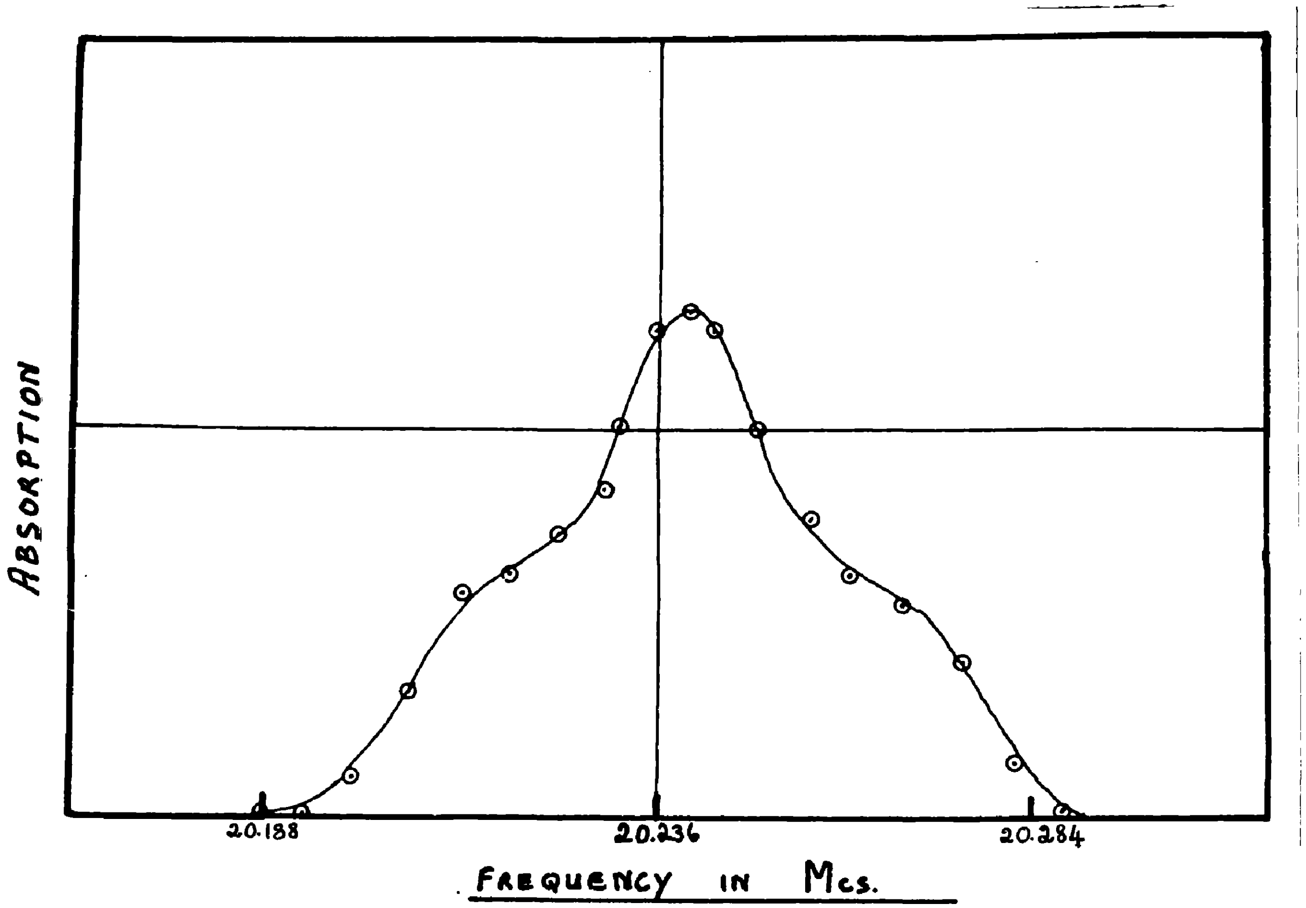
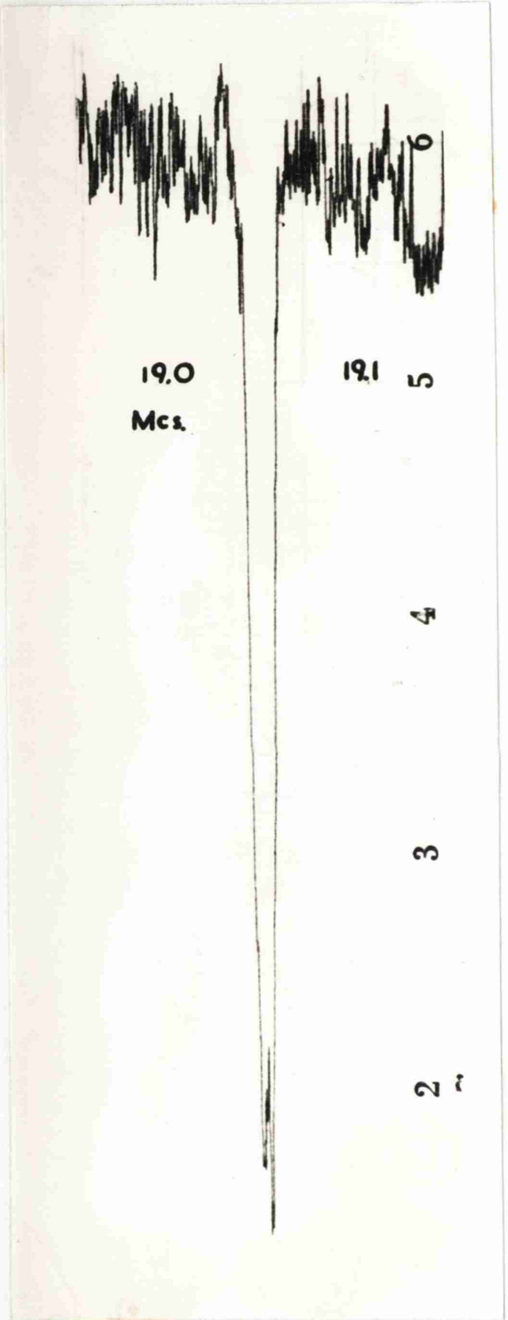


Figure 12

Proton Magnetic Absorption in Naphthalene plotted against frequency.

a dipole falls off with the inverse cube of the distance so that more distant neighbours contribute only a small amount to the local field.

Trace 2 shows a typical trace obtained of the proton resonance in ammonium fluoride at room temperature. The field modulation is held at a value less than the line width, and the first derivative with respect to the frequency is obtained for the nuclear absorption. The motor driven tuning condenser was used in obtaining this curve. Trace 3 shows the ^{31}P resonance in phosphonium iodide at room temperature. The paper speed was $\frac{1}{8}$" per minute and the sweep rate 1.8 Kcs/sec/min. The total line width between points of maximum slope was 5.4 Kcs/sec.



Trace 4

Reduction in the Proton N.M.R. Absorption in Ammonium Fluoride with saturation of the fluorine spin system.

(Zero Displaced)

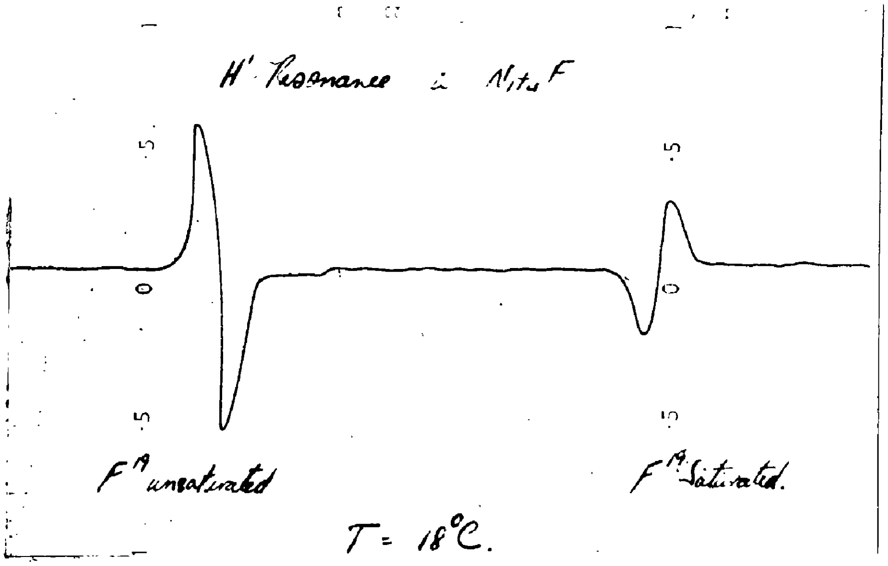
PART IV

The Overhauser Effect in the non-rigid Lattice

4.1 First Observation

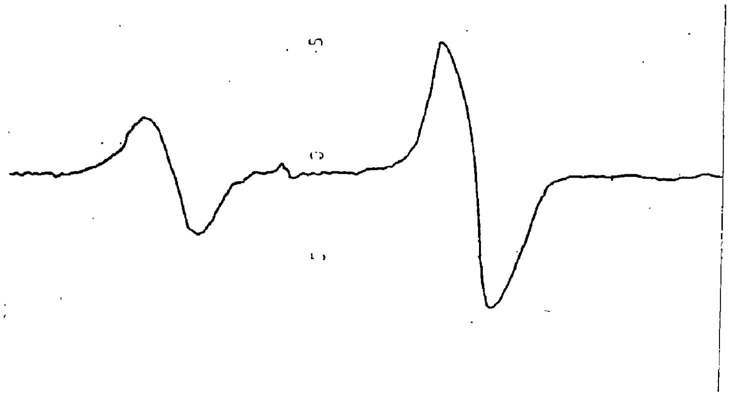
The Overhauser effect was first observed in ammonium fluoride at room temperature. The spectrometer was set at the peak of the nuclear absorption derivative signal. The saturating oscillator was turned on and the bridge balanced. The motor-driven tuning condenser slowly tuned the oscillator through the ^{19}F resonance while the pen-recorder traced the strength of the proton nuclear absorption. Trace 4 was obtained. The proton absorption fell to approximately $\frac{1}{2}$ when the ^{19}F spin system was saturated.

A second experiment was carried out to check this result. The saturating oscillator was slightly de-tuned from the ^{19}F resonance. A trace of the proton absorption was then taken. The ^{19}F spin system was then saturated and a second trace taken. Trace 5 was obtained. The apparent change of phase of the two signals is due to the tuning condenser sweeping in the opposite direction for the two traces.



Trace 5

Overhauser Effect in Ammonium Fluoride.



Trace 6 (a) (b)

Overhauser Effect in Phosphonium Iodide.

4.2. Saturation Experiment

The ratio of the heights of the two curves obtained in the manner described above are plotted against the size of the saturating radio-frequency magnetic field in figure 13. This clearly shows the change of the proton absorption as the ^{19}F spin system approaches saturation. It also shows that the saturating oscillator could adequately saturate the ^{19}F resonance in ammonium fluoride at room temperature. At each temperature at which a measurement was made a curve similar to figure 13 was taken to ensure that the spin system was saturated.

4.3. Proton Saturation

It was thought that an anomalous result might be obtained if the proton spin system was partially saturated by the r.f. field from the spectrometer. A series of experiments as described in 4.1 were carried out at different r.f. levels of the spectrometer. The ratio obtained in each case is plotted in figure 14 against the square of the spectrometer voltage setting. The ratio appears to be independent of this parameter over a very wide range. Measurements were usually taken at a setting of 1.0 volts^2,

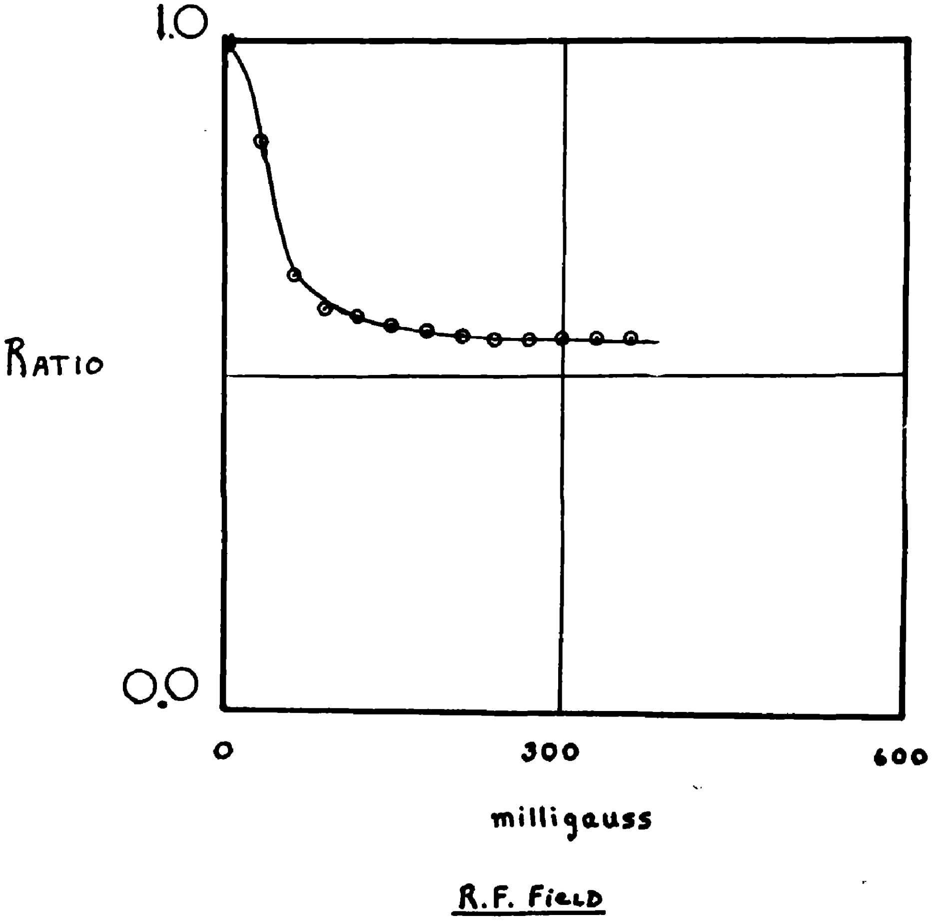


Figure 13

Decrease in Proton N.M.R. Absorption with saturation of fluorine spin system.

4.4. Ammonium Fluoride

The strength of the proton absorption in ammonium fluoride was measured at a number of different temperatures with the fluorine spin system saturated and unsaturated. The ratio of these two signals was plotted against the temperature. This is shown in figure 15(a). A number of different specimens gave quite different results. As it was known that NH_4F is highly deliquescent a specimen was carefully dried under vacuum and sealed in a pyrex tube. The curve 15(b) was obtained. This suggests that in the moist salt some other interaction bypasses the $^{1}H - ^{19}F$ interaction and maintains the protons in thermal equilibrium, in spite of the coupling to the saturated ^{19}F spin system. A comparison with the theory was not carried out for this salt.

In figure 16 a similar experiment is illustrated in which the ^{19}F resonance absorption was observed while the proton spin system was saturated.

4.5. Phosphonium Iodide

In order to compare the results of Part II

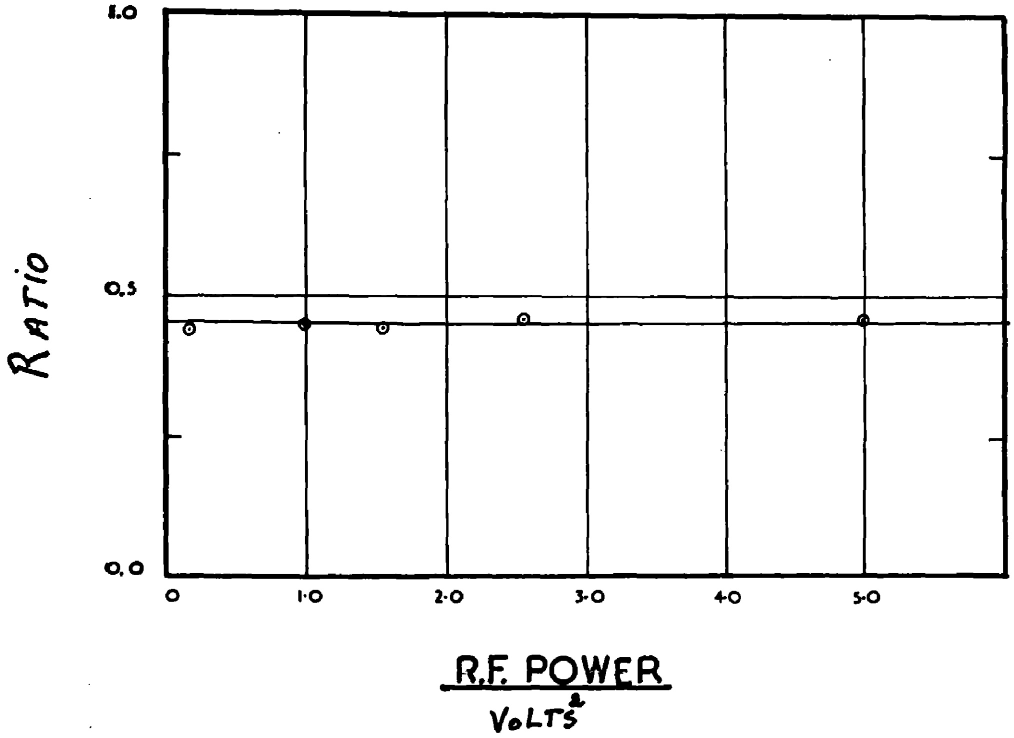


Figure 14

Overhauser Effect against Spectrometer Power in Volts^2.

with experiment some material was required for which the calculations of section 2.6 could be carried out. Ammonium fluoride was considered unsuitable for the reason given above. Phosphonium iodide was suggested as a suitable alternative.

The isotope ^{31}P is the only naturally occurring isotope of phosphorus. It has a spin $\frac{1}{2}$ and a magnetic moment approximately 0.4 of that of the proton. In phosphonium iodide the phosphorus atom is bound tetrahedrally to four hydrogen atoms. This forms the PH_4^+ ion.(Wells,1950) This ion has many of the properties of the ammonium ion. In particular, one could expect the ion to rotate in analogy to the rotation of the ammonium ion in the ammonium halides (Sachs and Turner,1951). In the ammonium halides the movement of the ammonium ion may be described in terms of a correlation time which has the following temperature dependence :

$$\tau_c = \tau_0 \exp\left(\frac{V}{KT}\right) \qquad \ldots 4.5.1$$

The potential V occurring in 4.5.1 is the height of the potential barrier which the molecule must

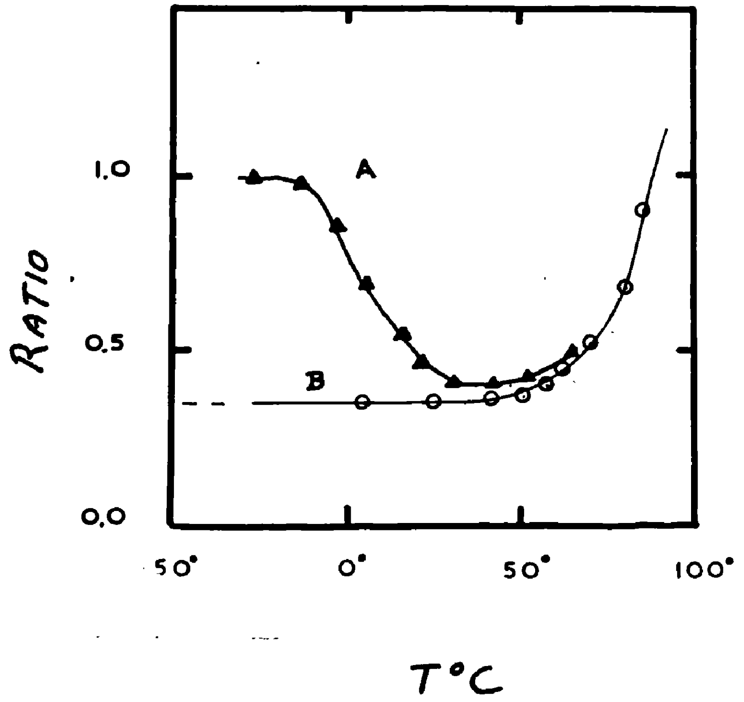


Figure 15

The Overhauser Effect in Ammonium Fluoride

A Moist Specimen

B Carefully dried Specimen.

Ratio of Proton Signal plotted with and without Fluorine spin system saturated against Temperature.

surmount in order to rotate to another equivalent position (Andrews,1955). One might expect a similar variation of the correlation time to occur in the phosphonium halides.

A 5 gm sample of phosphonium iodide was obtained from Messrs. Albright and Wilson. It was sealed in a specimen tube. The ^{31}P resonance was observed in the solid at room temperature. In trace 6a the signal from the ^{31}P resonance is shown. Trace 6b shows the enhancement of the ^{31}P signal due to the Overhauser effect obtained with the proton resonance saturated. Traces similar to these were taken at different temperatures in the range from -70°C to + 34°C. The temperature was not raised above this value because the salt is known to decompose at temperatures much above this. The low temperature limit was set by the difficulty of making accurate measurements much below the line width transition. A gradual broadening of the ^{31}P line occurs as the temperature is lowered below -65 °C. With the increase in the line width the signal becomes lost in noise.

In figure 17 the ratio of the signal , which is obtained with the proton spin system

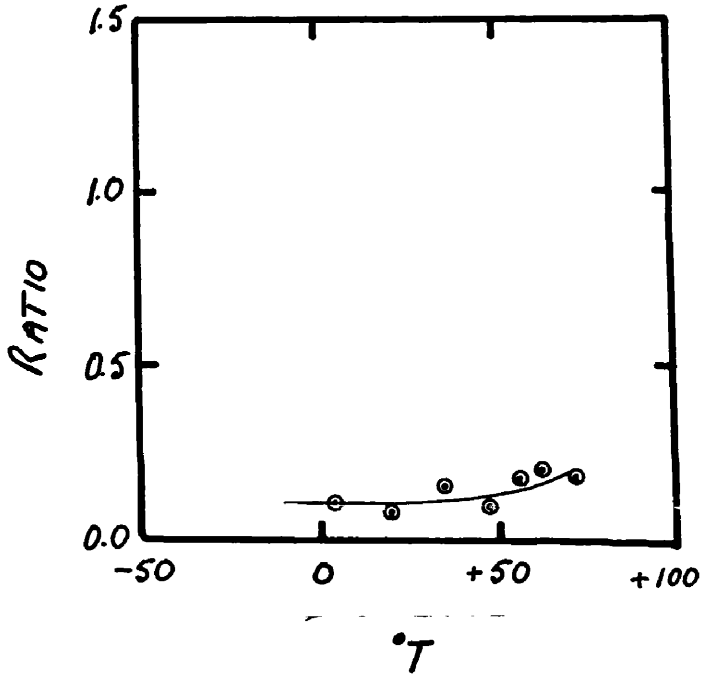


Figure 16

The Overhauser Effect on the Fluorine Spin System in Ammonium Fluoride.

Temperature Dependence.

Table 2

T °C	τ_c	Y_{+1}	Y_{-1}	Y_0	Ratio
+ 15	1.87×10^{-9}	0.283	0.050	0.150	2.22
+ 3	3.73	0.240	0.048	0.148	2.10
-4	5.27	0.200	0.046	0.144	1.97
-9	7.45	0.150	0.042	0.139	1.81
-22	1.75×10^{-8}	0.046	0.025	0.103	1.32
-28	2.59	0.023	0.016	0.075	1.17
-37	5.18	0.0061	0.0052	0.0300	1.06
-50	1.04×10^{-7}	0.0015	0.0014	0.0088	1.02

$$\tau_c = 9.8 \times 10^{-16} \times 10^{+1830/T}$$

Potential Barrier 8400 Cal/mole.

Multiply all Y's by $\left[\frac{2\tau_c}{\hbar^2} C_{\ell K}^2 \right]$

PHOSPHONIUM IODIDE

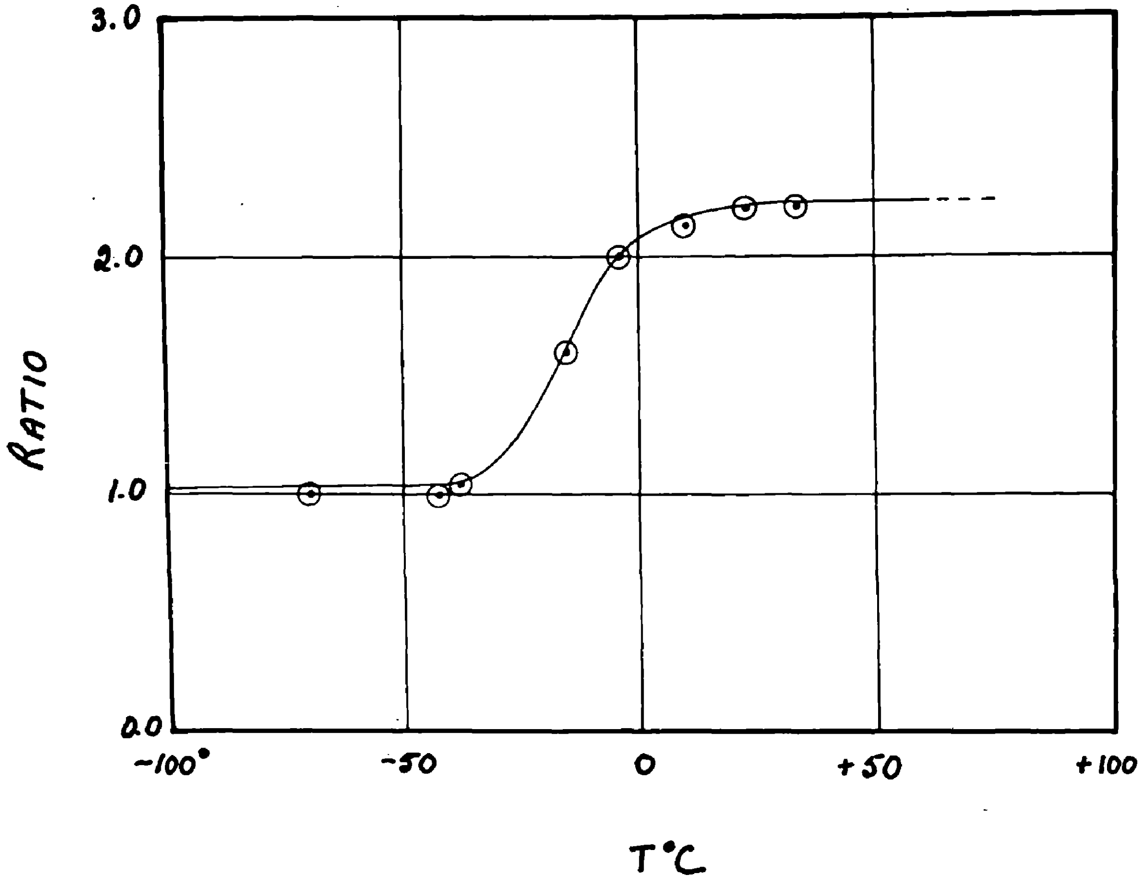


Figure 17

Overhauser Effect plotted against Temperature

Continuous Line-Theory

Points - Experiment.

PH_4I

saturated, to the signal with the proton spin system unsaturated is plotted against the temperature. The continuous curve was obtained by computing the Overhauser effect from the results of Part II section 2.6.

The calculation was performed by considering the interaction of the ^{31}P nucleus with the protons of the phosphonium ion. The P - H bond length is 1.43A and the P-I separation is 3.9 A (Wells,1950). The sum of the terms containing the P-I interaction amounts to 1/600 of the P-H interaction terms. For this reason the interaction of the protons alone was considered. It was assumed that the molecular correlation time could be described by an expression of the form 4.5.1 with $V = 8{,}400$ cals/mole and τ_0 9.8 x 10^{-16} secs. Table II gives the calculated values of each of the terms occurring in the summation of 2.6.16 and 2.6.17.

4.6. Discussion

The agreement with experiment is seen to be good. One criticism which could be levelled at the result is that one has two adjustable parameters with which to fit the experimental result. It should be noted, however, that these parameters do not determine the high or low temperature limits of of the theoretical curve. They only determine the temperature at which a transition from the low to the high temperature behaviour takes place and the slope of this curve at the transition. Furthermore, the value of the potential barrier is not in disagreement with similar results in the ammonium halides e.g.10,000 cals/mole in NH_4F (Drain,1955). The value of 9.8×10^{-16} sec.for the value of the correlation time extrapolated to very high temperatures appears to be appreciably shorter than similar results in NH_4Cl i.e. 2.6×10^{-14} sec. (Purcell, 1951). One might have expected this value to be nearer $1/2\pi\nu$, where ν is the frequency of rotation of the free ion. The fact that it differs appreciably from this value suggests that rotation is not the only way that the molecule can change its position. It is suggested that self-diffusion of the phosphonium ions occurs to an appreciable extent in the solid at room temperature. The potential barrier occurring in this case is of about the same height as that for the rotation of the ion. i.e.$\sim$8,000 cal/mole (Andrews, 1955) p. 174

A more exacting test of the theoretical results could be made if two experiments were carried out, the first to determine all the adjustable parameters and the second to test the theory. This has been

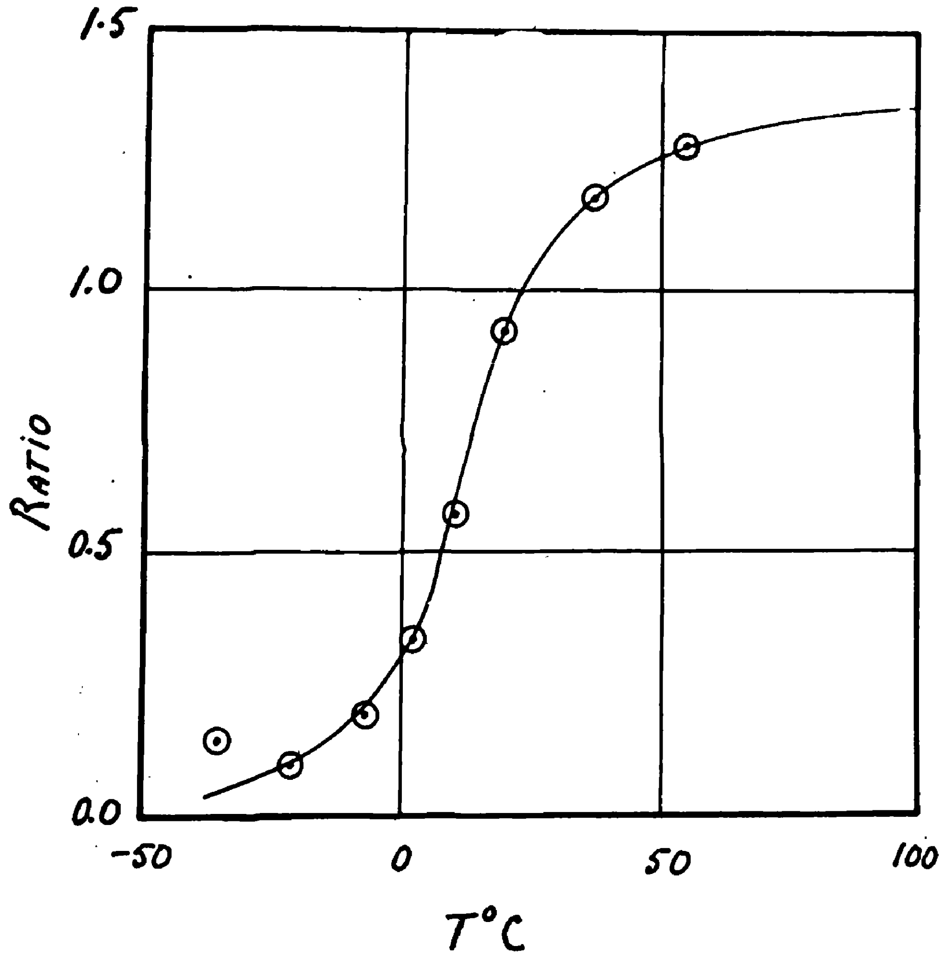


Figure 18

Change of Proton Polarisation in Ammonium Fluoborate with saturation of Fluorine Spin System.

Continuous Line - Theory.

Points - Experiment.

done for ammonium fluoborate.

4.7. Ammonium Fluoborate

Ammonium fluoborate has the structure of $BaSO_4$ (Wells,1950). The ammonium ions are located at the barium sites with the BF_4^- ions replacing the SO_4^{--} ions. The first experiment was carried out on the proton resonance with and without the fluorine spin system saturated. The ratio obtained is plotted against the temperature in figure 18. The theoretical curve was obtained by considering the interaction of the protons of tha ammonium group with the nitrogen nucleus and the twelve nearest fluorine nuclei.

The interaction of the protons within the ammonium ion is not included. The reason for this is that the total spin of the four protons of the ion is a good quantum number. The protons are identical and must obey Fermi statistics. In order for the total spin of the protons of the ion to change it is necessary for the rotational or vibrational quantum numbers to change at the same time. (Wilson, 1935). This will keep the state function for the ion anti-symmetric for an exchange of two protons. An interaction of the magnetic quadrupole form is required to bring about changes in the total spin. For this reason relaxation processes which depend upon this process are very weak compared to the magnetic dipole processes and may be neglected.

The orientation of the ammonium group in the unit cell is not known. In order to determine the separation of the hydrogen and fluorine nuclei it was necessary, then, to make an approximation. The fluorine nuclei lie almost evenly distributed on a sphere of radius 3.16 A with the nitrogen nucleus at the centre(Bragg, 1937). The four protons of the ammonium ion lie at 1.04A from the nitrogen nucleus (Gutowsky,Pake and Bersohn,1954). The mean value of $1/b^6$ was calculated, where b is the distance from a point on the inner sphere of radius 1.04A to a point on the outer sphere of radius 3.16 A.(See Appendix)

The value of 3.16A was arrived at by measuring the separation of the barium and oxygen atoms in $BaSO_4$. This came to a mean value of 2.95 A.

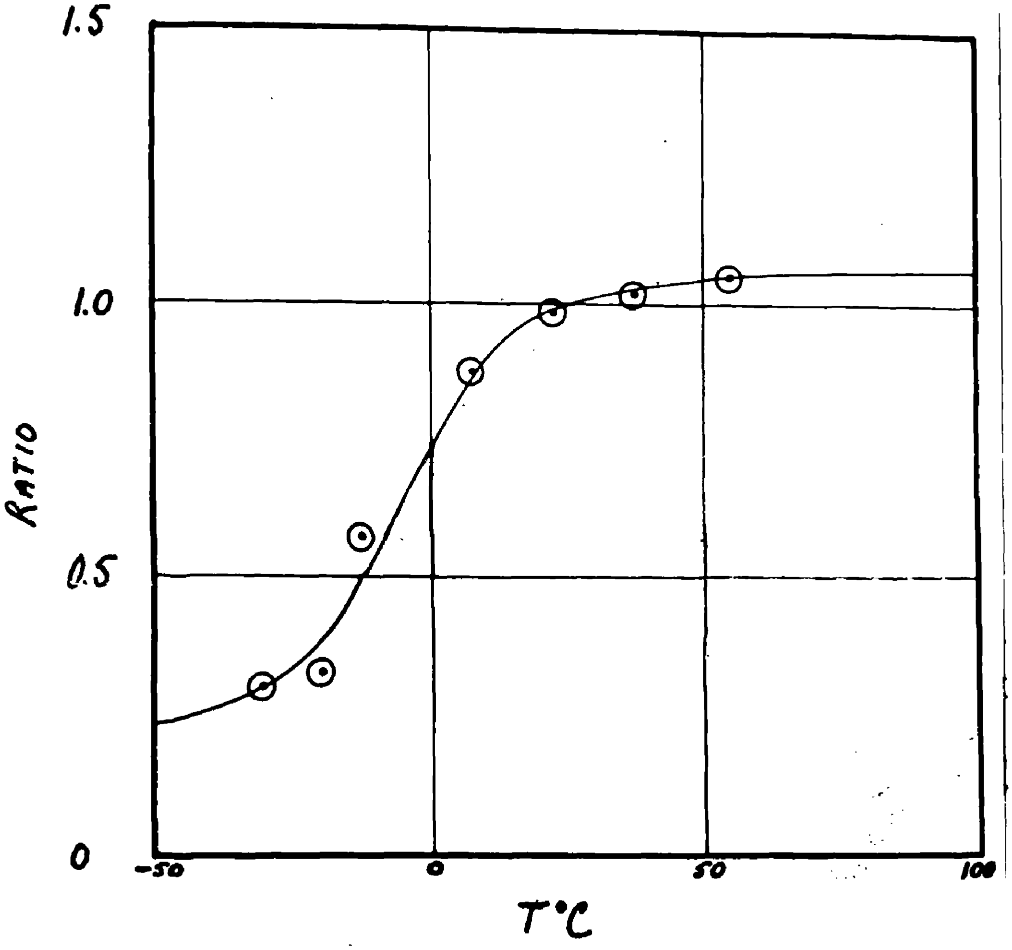


Figure 19

Change of Fluorine Polarisation with saturation of Proton Spin System in Ammonium Fluoborate.

Cohtinuous Line - Theory.

Points - Experiment.

A correction was then made for the difference in the size of the unit cell for NH_4BF_4 and also for the difference in the length of the S-O and the B-F bond lengths.

The experimental curve was fitted by assuming a value of 2.6×10^{-15} secs for τ_0 and a value of 9200 cals/mole for the height of the potential barrier.

The second experiment on ammonium fluoborate was carried out on the ^{19}F resonance with and without the proton spin system saturated. The B-F bond length was taken to be 1.4 A and the molecular correlation time was taken to be the same as that determined from the first experiment. The result obtained is shown in figure 19.

4.8. Conclusion

The theoretical and the experimental results are seen to agree for the non-rigid lattice. It might be argued that it is unlikely that the molecular correlatioh time should be the same for the movement of the ammonium ions and for the movement of the BF_4^- ions. However, if the movement of the lattice is due to self-diffusion of the molecules rather than a simple rotation, the mobility of the two ions might not differ by so much.

It should be noted that the transition probabilities which occur in calculating the Overhauser effect depends upon the separation of the interacting nuclei to the power of the inverse sixth. In favourable cases it is possible to measure the magnitude of the Overhauser effect to at least 1%. It should be therefore possible to measure the separation to better that 0.16%. An absolute measure of bond lengths cannot be made by this method but the ratio of two bond lengths can.

It is suggested that the Overhauser effect could be used in some crystals for resolving complex structures.

The behaviour of the Overhauser effect in the non-rigid lattice is seen to agree with the theoretical predictions of 2.6. In the next part the rigid lattice will be studied experimentally.

PART V

The Overhauser Effect in the rigid lattice.

5.1 Conditions

In order for a lattice to satisfy the conditions of rigidity set forth in 2.5 the spin correlation times must be short compared to the molecular correlation time. It was thought that triphenyl-phosphine might satisfy this condition. The molecule consists of three phenyl groups(C_6H_5) attached to the phosphorus atom. The large size and large moment of inertia of the molecule suggests that in the solid state it should not be able to move freely. The five protons of the phenyl groups are strongly coupled together owing to their close proximity. One could expect then a short spin-spin correlation time for the protons. This might provide the relaxation mechanism for the phosphorus nucleus.

An unsuccessful attempt was made to detect the phosphorus resonance at room temperature. A search was then made for the proton resonance. This was found to be very weak. The spin-lattice relaxation time for the protons was found to be about 20 seconds at room temperature. This is what one might have expected for a nearly rigid lattice.

No change was seen in the size of the absorption signal when the ^{31}P resonance was saturated. The result of 2.5 predicted that a reduction in the signal should have occurred.

In triphenyl-phosphine there is only one phosphorus nucleus to fifteen protons so that the average P-H interaction might be expected to be weak. A second experiment was then carried out using powdered LiF. In this material there are an equal numbers of lithium and fluorine nuclei. The ^{19}F resonance was observed while the ^{7}Li spin system was subjected to a saturating radio-frequency field. Again no effect was detected.

The failure of both the above experiments suggested that some other relaxation process was more important than the spin-spin interaction. Bloembergen (1949) and Rollin and Hatton (1948) had shown that paramagnetic impurities in an otherwise diamagnetic solid can provide a powerful relaxation mechanism for the nuclear spins. The nuclear spins which lie close to the impurity centres are strongly coupled to them. The impurities themselves are strongly coupled to the lattice due to the large electronic magnetic moment. Thus the nuclei lying close to the impurity centres are kept in thermal equilibrium. Due to the mutual spin-spin interaction, energy can diffuse to the impurity centres from the nuclei lying as many as 100 lattice spacings away. The energy is transferred by the mutual flip of two nuclear spins in which the energy and the angular momentum is conserved. In this way nuclei which lie a considerable distance from the impurity centres can be kept in thermal equilibrium by them.

It is suggested, therefore, that the reduction predicted by 2.5 is masked by the relaxation processes due to the presence of paramagnetic impurities. This could be checked by considering the dependence of the two processes upon the magnitude of the applied magnetic field.

The relaxation process which depends upon the presence of paramagnetic impurities should be practically independent of the applied magnetic field. The reason for this is that the effectiveness of the process is determined, principally, by the rate at which energy can diffuse to the impurity centres. This is determined by the nuclear spin-spin interaction. It does not depend upon the value of the applied magnetic field because energy is conserved in each mutual spin flip.

The relaxation processes required for 2.5, however, are dependent upon the value of the applied field. The transition probabilities may be written in the same form as 2.4.19 with the spin-correlation time τ_s replacing τ_c, the molecular correlation time. These transition probabilities are seen to decrease rapidly with increasing energy difference $\hbar\omega_{ij}$ between the initial and final states. This energy difference is proportional to the applied magnetic field.

It should be expected, therefore, that the predictions of 2.5 should not be masked by the presence of paramagnetic impurities at low values of the applied magnetic field. An experiment to check this was carried out.

5.2 Low Field Experiment

A single crystal 1" long and ½" in diameter of LiF was obtained from Barr and Stroud Ltd. The ^{19}F spin system in this crystal was found to have a spin-lattice relaxation time of 36 seconds at room-temperature in a field of 3600 gauss.

The bridge box was modified. The spectrometer coil was wound on a paxolin tube which extended beyond the bridge box to a distance of 25 cm from the centre of the magnet. The crystal was cemented to a Tufnol rod and could slide inside this tube. The fringing field of the magnet was measured. The crystal could be slid from the spectrometer coil to a predetermined position, where the magnetic field was known, by adjusting the position of a stop on the Tufnol rod.

5.3 Procedure

The spectrometer was set to the maximum of the ^{19}F absorption. The r.f. level of the spectrometer was held at a very low level in order to prevent saturation of the ^{19}F spin system. After the crystal had reached thermal equilibrium in the magnetic field it was removed to a position in the fringing field of the magnet and held there for a measured interval of time. It was then returned to the spectrometer coil and the absorption signal noted. The reduction of the signal was plotted against the time the crystal spent in the fringing

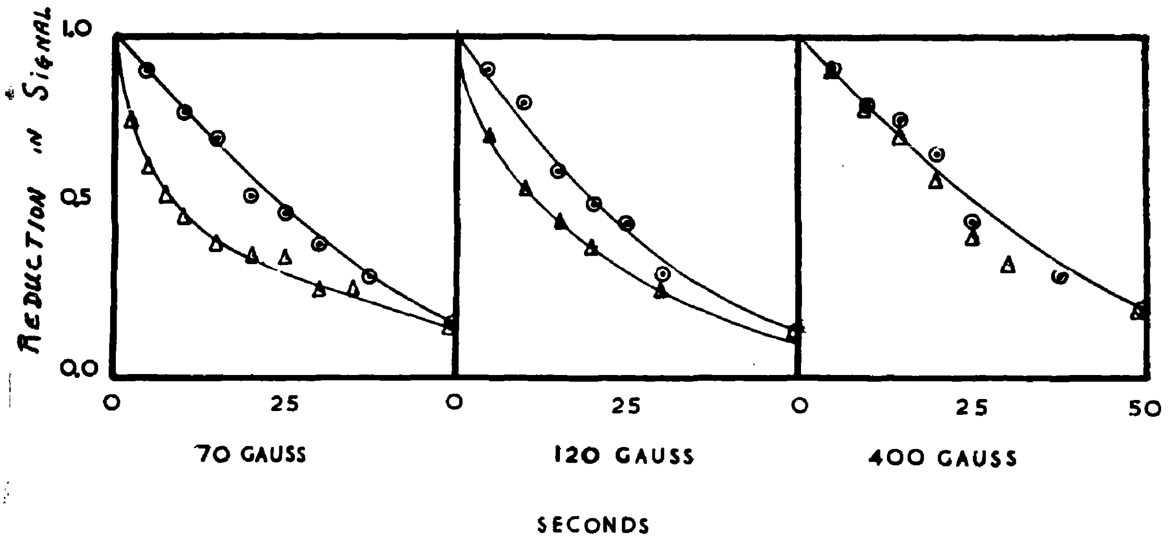


Figure 20

Low Field Experiment on LiF.

field.

This procedure was then repeated with the saturating oscillator tuned to the ^{7}Li resonance. The results obtained in each case are shown in figure 20. A series of experiments was carried out in which the crystal was held at different positions in the fringing field where the average magnetic field was 70, 120 and 400 gauss.

5.4 Discussion

At a field of 70 gauss with the ^{7}Li spin system saturated it is seen that the ^{19}F signal falls very rapidly at first. At higher field strengths the effect is less marked and at 400 gauss no appreciable effect is observed.

At 70 gauss the predictions of 2.5 are realised. The macroscopic magnetic moment of the ^{19}F spin system does not fall to zero, though, because in this case the ^{7}Li spin system does not remain saturated in the low magnetic field. As the ^{19}F spin system becomes heated through contact being made with the saturated lithium spin system, so the lithium spin system cools down. Equilibrium between the two spin systems is soon reached and the magnetism of both then decays away at about the same rate through contact with the paramagnetic impurities.

The experiment carried out here demonstrates the effect in a slightly indirect manner. Ramsey and Pound (1951) have described an experiment in which the effect is more directly demonstrated. They observed a reduction in the ^{7}Li absorption signal in LiF when the ^{19}F spin system was saturated in a field of 42 gauss.

PART VI

Conclusion

The most important conclusion which may be drawn from the results is contained in the work on the rigid lattice. At temperatures near 1°K the conditions of the rigid lattice are most likely to be satisfied. The lattice motion would be nearly completely frozen out. The spin-spin interaction would be large and the spin-correlation time short. It is to be expected, therefore, that the only effect of applying a saturating r.f. field to the electron spin resonance in a paramagnetic solid at these temperatures would be to reduce the nuclear spin polarisation to zero. This does not apply to a metal, of course, for in this case the time-dependent contribution to the Hamiltonian comes from the movement of the conduction electrons rather from a re-arrangement of the individual electron spins.

It would seem worthwhile then to consider whether a similar effect to the Overhauser effect could be obtained in non-metals by some other means. A number of suggestions on these lines are put forward in the next sections. Again they may be listed as dynamic or static methods.

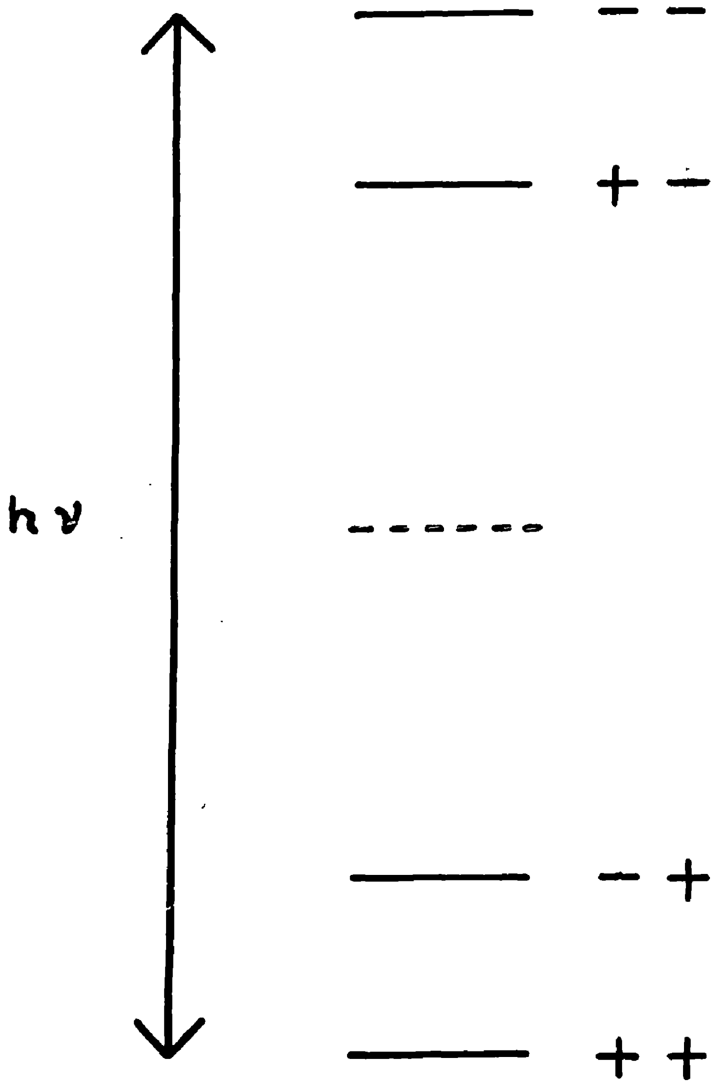


Figure 21

Energy Levels of a Pair

6.1 Dynamic Methods

Ultrasonic Technique

Consider a system of two particles which interact with one another. The energy levels of the system in a magnetic field H may be described by the diagram of figure 21. The populations of the levels will decrease with energy according to the Boltzmann distribution. The population of the levels will be approximately:

$$\begin{aligned} N_{--} &= \left[1 - (\mu_s + \mu_I)H/kT\right].N \\ N_{+-} &= \left[1 - (\mu_s - \mu_I)H/kT\right].N \\ N_{-+} &= \left[1 + (\mu_s - \mu_I)H/kT\right].N \\ N_{++} &= \left[1 + (\mu_s + \mu_I)H/kT\right].N \end{aligned} \qquad \ldots\ 6.1.1,$$

where N is a constant. It has been assumed that the Zeeman energies are all small compared to kT.

Suppose now that the solid is strongly irradiated with ultrasonic radiation of frequency ν corresponding to a transition as shown. The population of the $(++)$ and the $(--)$ states will be made equal. It should be noted that transitions of this type are allowed even though they correspond to a change of angular momentum of $2\hbar$. This can be readily seen from the Hamiltonian 1.4.10. The time-dependent part of the Hamiltonian is now provided by the accoustic vibration of the lattice which varies the separation of the two particles. A radiation field, on the other hand, would not allow transitions of this type to occur in the dipole approximation.

The spin polarisation of the spin I particles is given by :

$$P = \frac{(N_{++} + N_{-+}) - (N_{+-} + N_{--})}{(N_{++} + N_{-+}) + (N_{+-} + N_{--})} \qquad \ldots\ 6.1.2.$$

Under ultrasonic saturation this gives :

$$P = \frac{1}{2}(\mu_s - \mu_I)\, H/kT \qquad \ldots\ 6.1.3,$$

while in thermal equilibrium one obtains instead :

$$P = \frac{\mu_I H}{kT} \qquad \ldots\ 6.1.4.$$

One finds a spin polarisation which is $\frac{1}{2}$ of that obtained in metals by the Overhauser effect.

It is necessary in this case, though, to be able to resolve the transitions in which the angular momentum of the pair change by 0,1 and 2. Some idea of the ultrasonic power required may be obtained from the following approximate calculation. The probability for the proton to absorb or emit energy to the lattice has been calculated for the proton-electron system. If the proton is separated from the electron by a distance of 7A and the lattice is vibrating with an amplitude of 1 part in 10^4 the transition probability for the proton will be 0.1/sec.

For this technique an ultrasonic transducer capable of working at 10,000 Mcs/sec would be required. It would be necessary to know more of the attenuation coefficient of accoustic vibrations of this frequency before a reliable assessment of this technique could be made.

Optical Technique

The reason why most matter is diamagnetic is that in the ground state of the molecules of which the matter is composed the electrons pair off so that their resultant spin is zero. Whenever a free spin remains then the material becomes paramagnetic.

It is to be expected, therefore, that the excited state of a molecule could be paramagnetic. In organic phosphors such as anthracene the lifetime of the excited state is of the order of 10^{-8} second. (Birks and Little, 1953).

Consider what happens if the molecule in the $^1S_0$ ground state is excited with circularly polarised light in the positive sense. If the lifetime of the excited state is short compared to the time the three m-states take to reach thermal equilibrium amongst themselves then on the average only the +1 m-state will be appreciably populated. This corresponds to almost 100% polarisation of the electron spins. In a rigid lattice this spin polarisation of the electrons will be transmitted to the nuclear spin system through the spin-spin interaction. A high degree of nuclear polarisation could be then obtained.

In this technique only moderately low temperatures are required. These are only required in order to ensure that the lattice is effectively rigid. The energy of the optical radiation is large compared to kT at room temperature so that a negligible fraction of the molecules are normally in the excited state.

Some idea of the light intensity which would be required can be gathered from the following example. Let there be 10^{24} nuclei of spin $\frac{1}{2}$ and let their spin-lattice relaxation time be 10^{4} seconds. It would be necessary then to flip each spin at least once in this time in order to make an appreciable change to the equilibrium population of the spin states. Each quantum of radiation carries one unit of angular momentum so 10^{20} quanta/second would be required. This assumes that all the absorbed angular momentum is transferred to the nuclei. Suppose the coupling mechanism was only 1% efficient then 10^{22} quanta/second would be required. If the radiation must be in the ultraviolet each quantum of radiation will have an energy of something like 5×10^{-12} erg. The total input of energy would then have to be 5×10^{10} ergs/sec. or 5 Kilowatts.

The problem would then resolve itself into two parts. Firstly, the specimen would have to be efficiently cooled, and, secondly, an exceptionally powerful light source would be required together with efficient optical components for polarising the light.

It is worth noting one point about this method. If the specimen was used as a target for nuclear scattering experiments then nuclear particles would leave damage centres and F centres in their tracks. These would be paramagnetic and would soon reduce the spin-lattice relaxation time of the target nuclei. This would reduce in time the maximum spin polarisation which could be obtained.

6.2 Static Method

The total state-function for a molecule containing two or more identical particles in equivalent positions must be anti-symmetric for an exchange of any two of these particles if they obey Fermi statistics (Wilson,1935). For this reason certain combinations of the nuclear spin can only occur in certain rotational or vibrational states of the molecule (e.g. ortho-and para-hydrogen). It is sometimes possible to separate the different symmetry species of the molecule by means of thermal diffusion. This has been done for ortho- and para-hydrogen by Schäfer and Corte (1946). In a magnetic field H at a temperature T°K the spin polarisation would be $\frac{1}{3}\frac{(I+1)\mu_I H}{I k T}$. The total spin of the group of identical nuclei in the molecule cannot change without a corresponding change in the rotational or vibrational state which preserves the symmetry of the molecule. The orientation of this total spin I can change in magnetic dipole relaxation processes. For this reason I and μ_I which determine the spin polarisation are those of the total spin and total magnetic moment of all the identical nuclei. In certain symmetry species of the molecule all the n identical nuclei have their spins parallel. The spin polarisation in this species of the molecule will be $\left(\frac{nI+1}{I+1}\right)$ times greater than that for an equilibrium mixture of the symmetry species. Magnetic quadrupole relaxation processes bring about the inter-conversion of the different symmetry species. However, this proceeds at a much slower pace than the relaxation processes due to magnetic dipole interactions.

The increase of the nuclear spin polarisation attainable by this method depends upon the existence of molecules with a large number of equivalent nuclei. For the proton one could suggest hydrogen, methane and benzene with 2, 4 and 6 equivalent protons.

The feasibility of the method depends upon the effectiveness of separating the different symmetry species of the molecule. The rate of interconversion of the different species would have to be slow. One might expect this to be the case for the interconversion of ortho- and para-hydrogen proceeds at the rate of only a small percentage per hour. This is provided that it is kept free of paramagnetic catalyst.

6.3 Conclusion

Perhaps the greatest advance which could be made towards the attainment of the goal of producing polarised nuclear spins would be the discovery of some means for producing and maintaining temperatures an order of magnitude lower than those at present attainable through adiabatic demagnetisation. Recently such a technique has been suggested by London (1956). It might be possible to obtain a similar result by the adiabatic demagnetisation of a metal in which the nuclear spins had been aligned by the Overhauser effect. It remains to be seen whether either of these methods will be experimentally successful.

Appendix I

The step from 2.2.11 to 2.2.12 is not obvious. After summing over Θ (jt) and Π (fu) one may re-write 2.2.11 as :

$$\sum_{M'} \sum_{W} \sum_{s's} \left[\langle m's' | \sigma | m's' \rangle e^{*} \sum_{\ell} (m's' | I_{\ell}^{\tau} | ms) - (ms | \sigma | ms) (ms | I_{\ell}^{\tau} | m's') \right]$$

... I.1.1,

where e^{*} has been written for the exponential terms of 2.2.11. $W_{NN'}$ has been written as $\sum_{\ell}' (m's' | I_{\ell}^{\tau} | ms)$ to indicate that the transition probabilities depend upon the 1^{st} I particle. Each term in the above expression is positive or zero. Therefore we can consider each configuration s' separately. The matrix element $I_{\ell m}^{\tau}$ which occurs in the transition probability will be zero for all terms except for one particle I_{ℓ} . This can be seen from 2.2.8. The matrix element for this term will be $I_{\ell m}^{\pm 1} = \sqrt{(I \mp m_s)(I \pm m_s + 1)}$, where m_s is the initial m-state of the 1^{st} I particle. This element is either 0 or 1 for $I = \frac{1}{2}$. It connects m to m' = m + 1 or to m' = m − 1. Therefore, one may write

$$\frac{\langle ms / \sigma / ms \rangle}{\langle m-1, s' / \sigma / m-1, s' \rangle} = \frac{\sum_{W} e^{*} \sum_{\ell} (m-1, s' | I_{\ell}^{\tau} | ms)}{\sum_{W} \sum_{\ell} (m-1, s' | I_{\ell}^{\tau} | ms)}$$

... I.1.2.

The average value of this for the different arrangements s and s' give one :

$$\frac{\langle m|\sigma|m\rangle}{\langle m-1|\sigma|m-1\rangle} = \frac{\sum_{w} e^{*} \sum_{ss'} \sum_{\ell} (m-1, s' | I_{\ell}^{\tau} | ms)}{\sum_{w} \sum_{ss'} \sum_{\ell} (m-1, s' / I_{\ell}^{\tau} / ms)}$$

... I.1.3.

This is the result which is given in more familiar form in 2.2.12.

Appendix II

The Binomial Expansion

The degeneracy of a particular m-level is given by $g_m = \binom{n}{\frac{n}{2}-m}$. From the binomial expansion one obtains the relation :

$$\left(1+e^{\alpha}\right)^{n} = \sum_{m=+\frac{n}{2}}^{m=-\frac{n}{2}} \binom{n}{\frac{n}{2}-m} e^{\alpha\left(\frac{n}{2}-m\right)}$$

... II.1.1,

and hence :

$$\sum_{m} \binom{n}{\frac{n}{2}-m} e^{-\alpha m} = e^{-\frac{\alpha n}{2}} \left(1+e^{\alpha}\right)^{n}$$

... II.1.2.

This summation is used in the denominator of equation 2.2.18. In order to obtain the summation of the numbrator one must differentiate II.1.2 with respect to α . Multiplying this by -1 one obtains II.1.3.

$$\sum_{m} \binom{n}{\frac{n}{2}-m} m\, e^{-\alpha m} = \frac{n}{2} e^{-\frac{\alpha n}{2}} \left(1+e^{\alpha}\right)^{n} \left[\frac{1-e^{\alpha}}{1+e^{\alpha}}\right]$$

... II.1.3.

Therefore, 2.2.18 gives :

$$\frac{\gamma\hbar \sum_{M} \binom{n}{\frac{n}{2}-m} m\, e^{-\alpha m}}{\sum_{M} \binom{n}{\frac{n}{2}-m} e^{-\alpha m}} = \frac{n\gamma\hbar}{2} \left[\frac{1-e^{\alpha}}{1+e^{\alpha}}\right] = \bar{\mu}$$

... II.1.4

Provided that α is small the exponentials may be expanded to give

$$\bar{\mu} = -\frac{\hbar\gamma n}{4}\alpha$$

... II.1.5.

Appendix III

The transition probabilities of equation 2.6.1 may be computed as follows. The spin correlation times are both long compared to τ_c. Thus one may write the transition probability concerning the 1^{th} I particle and the k^{th} S particle as :

$$W_{NN'} = \overline{\left|I^{\tau}_{\ell m}\right|}^{2} \, \overline{\left|S^{\nu}_{kj}\right|}^{2} \frac{1}{\hbar^{2}} \left[\int_0^t \langle n' \,|\, \overline{F^{\tau\nu}_{\ell k}(t')} \,|\, N\rangle \, e^{-i\omega_{ij}t'} dt'\right] \times$$

$$\times \left[\int_0^t \langle n' \,|\, F^{\tau\nu *}_{\ell k}(t'') \,|\, n\rangle \, e^{+i\omega_{ij}t''} dt''\right]$$

... III.1.1,

where $\omega_{ij} = (\tau\gamma_I + \nu\gamma_S) H_0$

... III.1.2.

Inserting the correlation time from 2.4.3 and putting $t' - t'' = \tau$ one may change the variable of the integration to obtain :

$$\frac{1}{tK^2} \left| I^{\tau}_{lm} \right|^2 \left| F^{\tau\nu}_{lK}(0) \right|^2 \left| S^{\nu}_{Kj} \right|^2 \int_0^t dt' \int_{-\infty}^{\infty} e^{-\frac{|\tau|}{\tau_c}} e^{-i\omega_{ij}\tau} d\tau$$

III.1.3.

The integral is done in two parts :

$$\int_0^t dt' \int_{-\infty}^{\infty} e^{-\frac{|\tau|}{\tau_c}} e^{-i\omega_{ij}\tau} d\tau = \int_0^t dt' \left[\int_0^{\infty} e^{-\frac{\tau}{\tau_c}} e^{+i\omega_{ij}\tau} d\tau + \int_0^{\infty} e^{-\frac{\tau}{\tau_c}} e^{-i\omega_{ij}\tau} d\tau \right]$$

... III.1.4

This immediately gives the required result of equation 2.6.1.

Appendix IV

The matrix elements of $J^{\pm}$ are $\sqrt{(J \mp m)(J \pm m+1)}$ (Andrews,1955). The sum over all the initial m-states of $|J^+|^2$ gives :

$$\sum_m |J^+|^2 = \sum_m (J^2 + J - m^2 - m)$$

$$= (2J+1)(J+1)J - \sum_m m^2 - 0$$

$$= 2/3\ J(J+1)(2J+1)$$

and similarly for $\sum_m |J^-|^2$.

The summation for $\overline{|J^0|}^2$ is straight forward.

$$\sum_m{}' \overline{|J^0|}^2 = \sum_m{}' m^2 = 1/3\ J(J+1)(2J+1)$$

The average values of the $\overline{|F_{1k}|}^2$ have been calculated by Solomon (1955).

Appendix V

The fluorine atoms in NH_4BF_4 lie on a sphere of radius r_1 (3.16A) with the nitrogen nucleus as centre. Each proton of the ammonium ion lies at a distance of r_2 (1.04A) from the nitrogen nucleus. The exact position of each ^{19}F nucleus with respect to each proton is not known. It will be assumed that the probability of finding a fluorine nucleus at any point on the sphere is given by a density ρ / unit area. Then $\frac{\rho}{4\pi r_1^2} = n$. In ammonium fluoborate $n = 12$.

The Y_{12} of 2.6.3 will be proportional to

$$\frac{1}{b_{eff}^6} = \int \frac{1}{b^6} P(b)\, db \qquad \ldots \text{V.1.1,}$$

where $P(b)$ is the probability of a fluorine nucleus being at a distance b from the proton. The transition probabilities will be the same as that due to a single fluorine nucleus situated at a distance of $b_{eff.}$ from each proton.

b_{eff} may be calculated by putting in the value of $P(b)$ and the value of b in equation V.1.1.

$$\frac{1}{b_{eff}^{6}} = \int_{\theta=0}^{\theta=\pi} \frac{\frac{N}{2}\sin\theta\, d\theta}{\left(r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta\right)^3}$$

$$= \quad n\,\frac{\left(r_1^2 + r_2^2\right)}{\left(r_1^2 - r_2^2\right)^4} \qquad \ldots \text{V.1.2.}$$

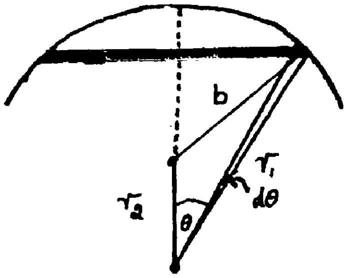


Figure 22

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