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DOCTOR OF PHILOSOPHY

of

HARALD WESEMEYER
Cand. Phys., Universitat Hamburg 1950
Diplom-Physiker, Universitat Hamburg 1953

IN ROOM 300, PHYSICS BUILDING

TUESDAY, APRIL 29, 1958 at 10:30 a.m.

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A paramagnetic resonance spectrometer operating at 3.2 cm has been built for use at liquid helium temperatures. This spectrometer employs a high Q transmission type cavity resonator which is equipped with windows on the broad faces to pass light through. The pole pieces of the electromagnet have axially centered holes for passing light through, too. This enables magneto-optical effects and paramagnetic resonances to be studied simultaneously. A high power klystron, and a high Q cavity resonator permit experiments with microwave power saturation.

The influence of the paramagnetic resonance absorption saturation on the paramagnetic Faraday effect has been studied. The paramagnetic Faraday effect (i.e. the rotation of the plane of polarisation of light passing through a paramagnetic crystal in the direction of an external magnetic field) is proportional to the magnetic moment of the crystal. When the crystal is exposed to microwave radiation of the correct frequency to cause appreciable saturation of this resonance, the magnetic moment is reduced, and a reduction of the rotation angle should be noticed. This effect was predicted by A. Kastler 1951, and a theory of this effect has been developed by W. Opechowski 1953.

This effect was found in Nd(C₂H₅SO₄)₃.⁹H₂O at 1.4°K. In this salt the magnetic moment is proportional to the difference of the populations of the two levels Ms = ± 1/2 of the Nd⁺⁺⁺ ion, having an effective ground state of S' = 1/2. Saturation levels of about 52%, 88%, and 100% were obtained and hence the rotation angle of the plane of polarisation reduced accordingly. Thus the effect predicted by A. Kastler has been established.

From the known power levels of the applied microwave frequency radiation the electron spin-lattice relaxation time of the Nd⁺⁺⁺ ions in the upper level was found to be about 1/20 s. at 1.4°K.

(CN₃H₆)Al(SO₄)₂.⁶H₂O, a crystal with trigonal structure, having 3 Al⁺⁺⁺ ions in the unit cell, has recently been discovered to be ferroelectric. The ferroelectric direction is along the trigonal axis. The determination of the structure was not completed when this work was started.

In order to complete the crystallographic data with respect to the crystalline field of the immediate neighbours of the Al⁺⁺⁺ ions, Cr⁺⁺⁺ ions were introduced into the lattice replacing Al by 2%, and then the resonance spectrum of the Cr⁺⁺⁺ ions investigated at 295°K, 195°K, 77°K, and 35°K. Two sets of axially symmetric spectra, a total of six lines were observed, set 1 being twice as intense as set 2. The investigations show that the Cr⁺⁺⁺ ions are exposed to a trigonal field. All three ions lie on the threefold axis, and since there are 3 ions per unit cell, two of them are magnetically equivalent. Both sets of spectra can be fitted to the
Spin-Hamiltonian

\[ \mathcal{H} = g \beta H \cdot S + D \left[ S^2 - \frac{1}{3} S(S + 1) \right] \]

where \( S = 3/2 \). The exact Hamiltonian was diagonalized using a digital computer, and the predicted lines agree with the measured ones within 1%. It was found that the \( D_1 \) and \( D_2 \) increase linearly with decreasing temperature, \( D_1 \) from \((0.0576 \pm 0.0005) \text{ cm}^{-1}\) at 295\(^\circ\)K to \((0.085 \pm 0.003) \text{ cm}^{-1}\) at 35\(^\circ\)K, and \( D_2 \) from \((0.0730 \pm 0.0003) \text{ cm}^{-1}\) at 295\(^\circ\)K to \((0.109 \pm 0.005) \text{ cm}^{-1}\) at 35\(^\circ\)K. \( g = 1.975 \pm 0.005 \) and stays constant over the range of the mentioned temperatures.

Further, ferroelectricity causes spontaneous distortion of the lattice, and this way may influence the paramagnetic resonance spectrum through changes in the crystalline field. Since different parts of a \((\text{CN}_3\text{H}_6)\text{Al(SO}_4)_3 \cdot 6\text{H}_2\text{O}\) crystal have different electrical properties, the spectrum of crystal fragments cleaved from different parts of a large crystal has been examined and no difference in the spectrum has been observed. The crystals were also polarised in a strong electric field along the trigonal axis and depolarised in a weakening alternating electric field with no effect on the spectrum. From this follows that the ferroelectric complex has very little effect on the immediate neighbours of the Cr\(^{+++}\) ions.

The paramagnetic resonance of Fe\(^{+++}\) in orthorhombic \((\text{NH}_4)_2 \left[ (90\% \text{ In, } 10\% \text{ Fe}) \text{Cl}_5 \cdot \text{H}_2\text{O} \right] \) has been investigated as this salt is interesting for adiabatic demagnetization. Noticeable signal strengths were obtained at about 25\(^\circ\)K only. The positions of the lines as functions of the rotation angles of the crystal about all three crystalline axes separately with respect to the magnetic field have been measured. In general four sets of equally intense spectra have been found for each rotation. From the maxima and minima of the curves of the spectra assuming the ions have axial symmetry it is possible to determine the direction cosines of the principal axes for the Fe\(^{+++}\) ions. These are

either \( l_1 = \pm 0.1860 \), \( l_1 = \pm 0.7576 \), \( l_1 = \pm 0.6636 \), \( l_1 = \pm 0.3289 \) or

\( l_2 = \pm 0.2212 \), \( l_2 = \pm 0.6357 \), \( l_2 = \pm 0.7123 \), \( l_2 = \pm 0.2762 \) or

\( l_3 = \pm 0.9578 \), \( l_3 = \pm 0.1488 \), \( l_3 = \pm 0.22805 \), \( l_3 = \pm 0.9033 \)

Because of the complexity of the spectra the spin-Hamiltonian has not yet been determined.
GRADUATE STUDIES

Field of Study: Physics

Quantum Mechanics ........................................... G. M. Volkoff
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PUBLICATIONS

Uber die Reinigung elektrolytisch polierter Metallflachen mittels Kathodenzerstaubung.
H. Wesemeyer and H. Raether, Die Naturwissenschaften 39 (1952), 398

Oberflachenuntersuchungen an elektrolytisch polierten Kupfer-und Zink-einkristallen mittels Elektronenbeugung.
H. Wesemeyer, Thesis, (1953), Hamburg

Paramagnetic Resonance of Chromium in Guanidine Aluminum Sulphate Hexahydrate.

The Influence of Paramagnetic Resonance Saturation on the Faraday Effect.
EXPERIMENTS ON PARAMAGNETIC RESONANCE ABSORPTION IN CRYSTALS AT LOW TEMPERATURES

by

HARALD WESEMeyer

Cand. Phys., Universität Hamburg, 1950
Diplom-Physiker, Universität Hamburg, 1953

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We accept this thesis as conforming to the required standard

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EXPERIMENTS ON PARAMAGNETIC RESONANCE ABSORPTION IN CRYSTALS AT LOW TEMPERATURES

Abstract

A paramagnetic resonance spectrometer operating at 3.2 cm has been built for use at liquid helium temperatures. This spectrometer employs a high Q transmission type cavity resonator which is equipped with windows on the broad faces to pass light through. The pole pieces of the electromagnet have axially centered holes for passing light through, too. This enables magneto-optical effects and paramagnetic resonances to be studied simultaneously. A high power klystron, and a high Q cavity resonator permit experiments with microwave power saturation.

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This effect was found in \( \text{Nd(C}_2\text{H}_5\text{SO}_4)_2\cdot9\text{H}_2\text{O} \) at \( 1.4^\circ\text{K} \). In this salt the magnetic moment is proportional to the difference of the populations of the two levels \( M_S = \pm \frac{1}{2} \) of the \( \text{Nd}^{++++} \) ion, having an effective ground state of \( S = \frac{1}{2} \). Saturation levels of about 52\%, 88\%, and 100\% were obtained and hence the rotation angle of the plane of polarisation reduced accordingly. Thus the effect predicted by A. Kastler has been established.

From the known power levels of the applied microwave frequency radiation the electron spin-lattice relaxation time of the \( \text{Nd}^{++++} \) ions in the upper level was found to be about \( \frac{1}{20} \) s at \( 1.4^\circ\text{K} \).

Guanidine aluminium sulphate hexahydrate, \( (\text{CN}_3\text{H}_6)\text{Al(SO}_4)_2\cdot6\text{H}_2\text{O} \), a crystal with trigonal structure, having three \( \text{Al}^{+++} \) ions in the unit cell, has recently been discovered to be ferroelectric. The ferroelectric direction is along the trigonal axis. The determination of the structure was not completed when this work was started.

In order to complete the crystallographic data with respect to the crystalline field of the immediate neighbours of the \( \text{Al}^{+++} \) ions, \( \text{Cr}^{+++} \) ions were introduced into the lattice replacing \( \text{Al} \) by 2\%, and then the resonance spectrum of the \( \text{Cr}^{+++} \) ions investigated at 295°K, 195°K, 77°K, and 35°K. Two sets of axially symmetric spectra, a total of six lines were observed, set 1 being twice as intensive as set 2. The investigations show that the \( \text{Cr}^{+++} \) ions are exposed to a trigonal
field. All three ions lie on the three-fold axis, and since there are 3 ions per unit cell, two of them are magnetically equivalent. Both sets of spectra can be fitted to the spin-Hamiltonian

$$\mathcal{H} = g \beta H \cdot \mathbf{S} + D \left\{ S_z^2 - \frac{1}{3} S(S+1) \right\}$$

where $S = \frac{3}{2}$. The exact Hamiltonian was diagonalized using a digital computer, and the predicted lines agree with the measured ones within 1%. It was found that the $D_1$ and $D_2$ increase linearly with decreasing temperature, $D_1$ from $(0.0576 \pm 0.0005) \text{cm}^{-1}$ at $295^\circ\text{K}$ to $(0.085 \pm 0.003) \text{cm}^{-1}$ at $35^\circ\text{K}$, and $D_2$ from $(0.0730 \pm 0.0003) \text{cm}^{-1}$ at $295^\circ\text{K}$ to $(0.109 \pm 0.005) \text{cm}^{-1}$ at $35^\circ\text{K}$. $g = 1.975 \pm 0.005$ and stays constant over the range of the mentioned temperatures.

Further, ferroelectricity causes spontaneous distortion of the lattice, and this way may influence the paramagnetic resonance spectrum through changes in the crystalline field. Since different parts of a $(\text{CN}_3\text{H}_6)\text{Al}(\text{SO}_4)\text{Al}(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ crystal have different electrical properties, the spectrum of crystal fragments cleaved from different parts of a large crystal has been examined and no difference in the spectrum has been observed. The crystals were also polarised in a strong electric field along the trigonal axis and depolarised in a weakening alternating electric field with no effect on the spectrum. From this follows that the ferroelectric complex has very little effect on the immediate neighbours of the $\text{Cr}^{+++}$ ions.
The paramagnetic resonance of Fe\textsuperscript{+++} in orthorhombic ammonium penta chlorindate hydrate, (NH\textsubscript{4})\textsubscript{2}[In\textsubscript{10}Fe\textsubscript{7}Cl\textsubscript{5}.H\textsubscript{2}O] has been investigated as this salt is interesting for adiabatic demagnetization. Noticeable signal strengths were obtained at about 25\textdegree K only. The positions of the lines as functions of the rotation angles of the crystal about all three crystalline axes separately with respect to the magnetic field have been measured. In general four sets of equally intensive spectra have been found for each rotation. From the maxima and minima of the curves of the spectra assuming the ions have axial symmetry it is possible to determine the directional cosines of the principle axes for the Fe\textsuperscript{+++} ions. These are

\[ \ell = \pm 0.1860 \quad \ell = \pm 0.7576 \quad \ell = \pm 0.6636 \quad \ell = \pm 0.3289 \]
\[ m = \pm 0.2212 \quad m = \pm 0.6357 \quad m = \pm 0.7123 \quad m = \pm 0.2762 \]
\[ \kappa = \pm 0.9578 \quad \kappa = \pm 0.1488 \quad \kappa = \pm 0.22805 \quad \kappa = \pm 0.9033 \]

Because of the complexity of the spectra the spin-Hamiltonian has not yet been determined.
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representative. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

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Date Tuesday, April 29, 1958
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To Dr. J.M. Daniels I am especially very grateful for his guidance and help in every phase of the work, in theoretical and experimental problems and numerous discussions.

I am also thankful to Dr. M. Bloom and Dr. W.A. Little for many discussions.

The Department of Chemistry is thankfully acknowledged for its advice for the preparation of salts which I investigated.

The equipment used could not have been designed and constructed so adequately without the cooperation of Mr. H. Zerbst, technician in the Low Temperature Physics Laboratory, and the members of the workshop, particularly Mr. J. Lees, Mr. W. Maier, and Mr. A. Fraser.

Finally I wish to acknowledge the help of my wife, Beate, who has helped both by her constant encouragement and by her assistance in preparing the draft of this thesis.
KEY TO THE SYMBOLS AND THE SYSTEM OF UNITS WHICH ARE USED IN
THIS THESIS

The author has used the internationally adapted rationalized M K S system. Some physical quantities which are often used in this work are listed here. Occasionally, whenever it seemed to be necessary, data are given in both the M K S system and - in brackets - the symmetrical gaussian system for the convenience of comparison with other results.

For the units the following letters are used:

\[ m = \text{meter}, \ s = \text{second}, \ kg = \text{kilogram}, \ V = \text{volt}, \ A = \text{ampere}, \ W = \text{watt}, \ mW = \text{milliwatt}, \ W = \text{microwatt}, \ c/s = \text{cycles per second}, \ kc/s = \text{kilocycles per second}, \ Mc/s = \text{megacycles per second}, \ atm = \text{physical atmosphere}. \]

The field constants are

\[ \mu_0 = 4\pi \cdot 10^{-7} \frac{Vs}{Am}, \quad \varepsilon_0 = 8.8543 \cdot 10^{-12} \frac{As}{Vm} \]

The magnetic field is measured in A/m, the magnetic flux in Webers or Vs, the flux density in Vs/m². For the conversion of magnetic field units from one into the other system there are the relations:

\[ 1 \text{ Oe} = \frac{10^3}{4\pi} \frac{A}{m} = 79.577 \frac{A}{m}, \quad 1 \text{ Gauss} = 10^{-4} \frac{Vs}{m^2} \]

Bohr's magneton \( \beta = \mu_0 \frac{e}{2m} \) in Vs m where \( \hbar = \frac{\hbar}{2\pi} = 1.16 \cdot 10^{-34} \) Joule.s

Angular momentum \( \vec{P} = \sqrt{J(J+1)} \hbar \) in Joule.s

Magnetic moment \( \vec{\mu} = \gamma \vec{P} \) in Vs.m
where \( \gamma \) is the magneto-gyric ratio \( \gamma = \frac{g/\beta}{\hbar} \) in m/Coulomb. The potential energy of an atom with \( \vec{\mu} \) in a field \( \vec{H} \) is given by

\[
E_{\text{pot}} = E_0 - (\vec{\mu} \cdot \vec{H}) = E_0 - \mu H \cos \Theta
\]

Energy differences are given in Joule \( \Delta E = \Delta \nu = \gamma \beta H \)

Larmor precession \( \omega_L = \gamma H = \frac{\mu \beta}{\hbar} H \)

The frequency is sometimes given in wave numbers \( \nu = \frac{1}{\lambda} \) in cm\(^{-1}\).

The imaginary component of the radio frequency susceptibility of a paramagnetic salt has been rewritten for the MKS system:

\[
\chi''(\nu) = \frac{n}{\xi_0} \frac{g \beta^2 N_\nu \nu \mathcal{P}(\nu)}{8 \pi T} \left\{ \frac{s(s+1) - M(M-1)}{2 s + 1} \right\}
\]

where \( N_\nu \) is the number of dipoles per m\(^3\), \( g \) the splitting factor, \( \mathcal{P}(\nu) \) describes the line shape and is normalised by

\[
\int_0^\infty \mathcal{P}(\nu) d\nu = 1
\]
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I) INTRODUCTION

1.1) Electron Paramagnetism and Paramagnetic Resonances

In this thesis we deal with electron paramagnetism in the solid state, in particular with paramagnetic resonance absorption. At first we shall briefly outline the research field and then formulate the problem.

The paramagnetism of solids is characterized by an assembly of atomic magnetic moments regularly distributed over the crystal lattice and interacting with each other and with the non magnetic constituents of the crystal. The atomic magnetic moments are due to unpaired electrons of the atoms, and an atom in any energy state has a magnetic moment when the total quantum numbers $J \neq 0$. When an atom is chemically bound in a lattice it can only possess a magnetic moment if it has an incomplete inner shell. Hence paramagnetic compounds in the solid state contain elements of any of the following transition groups: the iron group (3d-shell), the palladium group (4d-shell), the rare earth group (4f-shell), the platinum group (5d-shell), and the actinide group (5f- and 6d-shell). Paramagnetism of semi-conductors, insulators with imperfections, (colour centres), substances containing free radicals will not be discussed here.

The presence of the elements of a transition group in...
a compound, however, does not always produce paramagnetism. In
covalent compounds each bond consists of a pair of electrons
with opposite spins. Electrons of unfilled inner shells
sometimes take part in covalent bonding, and hence these
electrons do not contribute to paramagnetism as they would in
ionic crystals.

Further, in bulk material of pure metals of these
groups the exchange forces between the magnetic moments are
great, and usually the exchange energy for magnetic moments
being aligned is negative which results in exchange magnetization.
For certain elements of the iron group the exchange energy for
magnetic moments being aligned is positive, and according to
Heisenberg we have exchange magnetization which results in
ferromagnetism. For the rare earth elements the exchange
energy is only slightly positive so that even a slight thermal
agitation is able to counteract the exchange magnetization,
and crystals of the rare earth elements are ferromagnetic only
near absolute zero.

We shall deal with ionic crystals only. In these the
paramagnetism is greatly influenced by the strong electrostatic
field in the lattice. The inner incomplete shell of a para-
magnetic ion is not well shielded by outer electron shells, and
in the iron group there is no shielding. The electrostatic
field acts on the orbital momentum of the electrons lifting a
part of the orbital degeneracy. Due to spin-orbit coupling
the magnetism arising from the electron spin is also affected
the crystalline field.
Paramagnetic properties of solids can be investigated by measurements of the susceptibility, of the Faraday effect, of the specific heat, by paramagnetic relaxation and paramagnetic resonance. All but the last of these methods study the bulk properties of matter. In ionic crystals the paramagnetic properties depend on the behaviour of the occupied lower electronic states, in particular their separation, their relative position, and their anisotropic behaviour in a magnetic field. Paramagnetic resonance as a spectroscopic method studies the paramagnetic properties from an atomistic point of view, and is a very sensitive method in comparison to the other methods. Paramagnetic resonance has, however, some disadvantage in investigation of paramagnetism. Certain substances cannot be investigated because there are no allowed transitions between the levels which give rise to paramagnetism or because the initial splitting of the ground state is already so great that an induced magnetic dipole transition cannot be obtained with microwave frequency. Because of the latter statement and because of the fact that only the lowest energy levels are populated, at present, information can be obtained only about the ground state.

Paramagnetic resonance absorption in paramagnetic crystals is only possible when the energy levels of the system of magnetic dipoles contributing to this resonance have different populations. When the magnetic dipole system and the lattice are in thermal equilibrium the energy levels are populated according to Boltzmann's distribution law. Interactions between
the spin system and the lattice maintain this equilibrium. The alignment of a system of spins also depends on interactions between them as will be discussed later.

The experiments described in this thesis are connected with the following two problems:

a) The influence of the crystalline electric field as to its strength and symmetry on the lowest energy levels of a paramagnetic ion.

b) The saturation of a paramagnetic resonance and its influence on the paramagnetic Faraday effect.

To the first problem two investigations are related.

The spectrum of Cr$^{3+}$ ions in a new ferroelectric compound has been studied at various temperatures. From the influence of the crystal field on the spectrum information about the crystalline electric field is obtained. The problem, the experiments and the spectrum are discussed in chapter IV.

In chapter V experiments on an orthorhombic salt containing Fe$^{3+}$ ions are described and discussed.

As to b) one problem was studied.

A series of experiments were carried out to study the influence of the paramagnetic resonance saturation on the Faraday effect. The results are discussed in chapter VI.

In the next sections the theory of paramagnetic resonance in solids is briefly outlined. Only those parts of the theory are emphasized which are later used in the discussion of the results.
The theory of the influence of paramagnetic resonance on the Faraday effect is not given in this chapter but is given as an introduction in chapter VI.

Chapter II briefly describes the experimental technique in paramagnetic resonances and chapter III the experimental apparatus, which was designed and built for the performance of the experiments.

1.2) Outline of the Theory of Paramagnetic Resonances in Solids

a) Introduction

The paramagnetic resonance absorption was discovered by Zavoisky in 1945 \(^1\). Shortly thereafter, an intensive research on this subject started in the Clarendon Laboratories at Oxford, England, and then at the University of Leyden in Holland. By now, paramagnetic resonances constitute a huge branch of physics, and very good review articles of this subject have been published. The first preliminary survey was given by Bagguley et al. 1948 \(^2\). It contains data on various salts of the iron group. Later in 1951 Elliott and Stevens \(^3\) published a review of paramagnetic resonance investigations of some rare earth ethylsulphates. An excellent summary of both the experimental and theoretical aspects is given in the review articles by Bleaney and Stevens \(^4\), and Bowers and Owen \(^5\).

Since this thesis is mainly concerned with experimental work we shall not report the theory here. We shall instead
indicate how a paramagnetic resonance spectrum is described and interpreted.

b) Description of a Paramagnetic Resonance Spectrum

The energy of the paramagnetic ion is described by a Hamiltonian usually written as the sum of a number of terms whose contribution to the energy of the ground state is in descending order of magnitude as

$$\mathcal{H} = \mathcal{H}_{\mu \mu} + \mathcal{H}_V + \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_H + \mathcal{H}_N$$  \hspace{1cm} (1)$$

where $\mathcal{H}_{\mu \mu}$ describes the energy of the free ion, $\mathcal{H}_V$ its interaction with the crystalline field, $\mathcal{H}_{LS}$ the spin-orbit interaction, $\mathcal{H}_{SS}$ the electronic spin-spin interaction, $\mathcal{H}_H$ the interaction of the ion with the external magnetic field, and $\mathcal{H}_N$ represents the hyperfine structure interactions which are not of interest here.

The order of precedence of these terms varies with the ion under consideration, and the descending order in formula (1) applies to the elements of the iron group. For the elements of the rare earth group the interaction of the crystalline field with the $4f$ electrons is much smaller than the spin-orbit coupling because of the partial shielding of the crystalline field by the outer electron shells, and hence $\mathcal{H}_V \ll \mathcal{H}_{LS}$.

The actual possible energy values are the eigenvalues which satisfy the operator equation $\mathcal{H} \psi = E \psi$, where $\psi$ represents the wave function of the state in question. An exact
solution is usually obtained for the largest term $H_m$, and the effect of the remaining terms is taken into account by perturbation calculations.

To calculate the perturbing part $H_v$ which represents the interaction with the crystal field potential, this potential is expanded in spherical harmonics. The number of terms is then skilfully reduced using orthogonality relations and symmetry properties of the electric field potential.

Then the matrix elements of the potential operators are expressed by equivalent matrix elements of angular momentum operators and the angular momentum operators are given by Wigner coefficients. The method of calculating the matrix elements of the field potentials has been discussed in details by Stevens.

It is difficult to calculate many of the other parameters involved in the total Hamiltonian. Furthermore, when they can be evaluated, the accuracy is poorer than can be obtained experimentally.

A semi-empirical Hamiltonian is therefore used which is called the "spin-Hamiltonian". It is based on the concept of an effective spin $S'$ which is obtained by equating the multiplicity of the lines observed to $2S' + 1$. The sum of all the terms, written as sum of energy operators to be applied to the effective spin states, constitutes the spin-Hamiltonian for the system.

The spin-Hamiltonian contains angular momentum operators and some constants which depend on the symmetry and
strength of the crystalline electric field, and the components of the spectroscopic splitting factor $g$ which is analogous to the Lande factor $g_L$, for a free ion, but in general has different values for an ion in a crystal. This is because the part of the magnetic moment arising from the orbital motion of the electron is modified by the crystalline electric field.

$$g = c \langle A_+ | L + 2 S | A_- \rangle$$

where $A_+$ and $A_-$ represent the states which are modified by the crystal field and $c$ is a constant.

Since the magnitude of the orbital part of the magnetic moment depends on the crystal field, $g$ shows an angular variation which follows the symmetry of the crystal field. This leads to an anisotropic $g$-value. If the external magnetic field $H$ has direction cosines $l, m, n$ with respect to the $x, y, z$-axes the $g$-value for this direction is

$$g = \sqrt{l^2 g_x^2 + m^2 g_y^2 + n^2 g_z^2} \quad (2)$$

The splitting of the effective spin-levels by the magnetic field $H$ only, is represented by the energy operator

$$H = \beta \left( g_z H_z S_z + g_x H_x S_x + g_y H_y S_y \right) \quad (3)$$

where $H_z, H_x, H_y$ are the components of the external magnetic field, $S_z, S_x, S_y$ the components of the spin angular momentum operator. Van Vleck, Pryce, Abragam and Pryce $^7$ have developed the following spin-Hamiltonian for the various interactions

$$H = \beta \left( g_z H_z S_z + g_x H_x S_x + g_y H_y S_y \right) + D \left( S_z^2 - \frac{1}{3} S(S+1) \right) + E \left( S_x^2 - S_y^2 \right) \quad (4)$$

The terms in $D$ and $E$ describe how the levels behave in zero
magnetic field and come from the second order effects of the crystalline field and spin-orbit coupling and from the spin-spin interaction.

In case of axial symmetry the spin-Hamiltonian reduces to

$$\mathcal{H} = \beta g_{\parallel} H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + \mathcal{D} \left\{ S_z^2 - \frac{1}{3} S(S+1) \right\} \quad (5)$$

where $g_{\parallel}$ and $g_{\perp}$ are the spectroscopic splitting factors parallel and perpendicular to the $z$-axis.

In strong fields where $g/\beta H \gg \mathcal{D}$, it is convenient to choose the axis so that elements in $S_x$ and $S_y$ do not occur in the major term $g/\beta H \cdot S$ of the spin-Hamiltonian. If $g$ is anisotropic the axis about which the spin precesses is chosen as the new $z$-axis. The question of angular variation has been treated in detail by Bleaney. When the magnetic field $H$ makes an angle with the symmetry axis of the crystalline electric field, the allowed electronic transitions with $\Delta M = \pm 1$ are given by

$$\hbar \nu = g/\beta H + \mathcal{D} (M - \frac{1}{2}) \left\{ 3 \left[ \frac{g_{\parallel}}{g} \right]^2 \cos^2 \Theta - 1 \right\}$$

$$- \left( \mathcal{D} \frac{g_{\parallel} g_{\perp}}{g^2} \cos \Theta \sin \Theta \right)^2 \frac{1}{2g/\beta H_o} \left\{ 4 S(S+1) - 24M(M-1) - 9 \right\}$$

$$+ \left( \mathcal{D} \left[ \frac{g_{\perp}}{g} \right]^2 \sin^2 \Theta \right) \frac{1}{8g/\beta H_o} \left\{ 2 S(S+1) - 6 M(M-1) - 3 \right\}$$

where $g^2 = g_{\parallel}^2 \cos^2 \Theta + g_{\perp}^2 \sin^2 \Theta$, $S$ is the spin quantum number, $M$ is the magnetic quantum number, and $H_o$ is the average magnetic field as defined below. As measurements are usually made at constant frequency with a varying field strength, the
equation above can be rearranged to give the position of the absorption lines directly in terms of the magnetic field. In the absence of a fine structure splitting, all lines would coincide at a field \( H = H_0 \). We define \( H_0 = \frac{\hbar \nu}{g \beta} \) and rewrite the equation in the form

\[
H = H_0 - \frac{D}{g^2} \left( M - \frac{1}{2} \right) \left\{ 3 \left( \frac{g_s}{g} \right)^2 \cos^2 \Theta - 1 \right\} + \frac{\left( \frac{D}{g^2} \right)^2}{2 \delta H_0} \left\{ \frac{g_s g}{g^2} \cos \Theta \sin \Theta \right\} \left\{ 4 S(S+1) - 24 M(M-1) - 9 \right\} - \frac{\left( \frac{D}{g^2} \right)^2}{8 \delta H_0} \left( \frac{g_s}{g} \right) \sin \Theta \left\{ 2 S(S+1) - 6 M(M-1) - 3 \right\}
\]  

(6b)

When \( \Theta = 0^\circ \) and \( H \) is along the crystalline axis, all the second order terms in \( D \) are zero, and hence the 2 S electronic transitions are equally separated in the magnetic field. The value of \( D \) can then be determined directly from this separation.

The first order variation of the spectrum with angle follows according to \( \left\{ 3 \left( \frac{g_s}{g} \right)^2 \cos^2 \Theta - 1 \right\} \), and thus the splitting falls to zero when

\[
\Theta = \arccos \frac{g}{g_s \sqrt{3}}
\]

At \( \Theta = 90^\circ \) there is a subsidiary maximum at which the lines are in reversed order as compared with their positions at \( \Theta = 0^\circ \).

Due to the second order term not all the lines cross at the same angle. When the symmetry of the crystalline field is not axial, we have to deal with additional terms as mentioned above in equation (4). Their effect is taken into account by second order perturbation. The method is outlined in Bowers and Owen where simple cases are worked out 5).
c) Line Width

The broadening of the absorption lines is mainly determined by the relaxation processes. The theory of these processes has been developed by Kronig \(^9\), and van Vleck \(^10\).

c. α) Spin-Lattice Interaction

Two relaxation processes are distinguished; the spin-lattice relaxation and the spin-spin relaxation. The line broadening due to spin-lattice relaxation is produced by the interaction of the paramagnetic ions with the thermal vibrations of the lattice. According to Kronig the spins interact via the spin-orbit coupling with the vibrating electric field of the lattice. The spins can either exchange a whole quantum of energy with the lattice vibration of the appropriate frequency (direct process) or transfer energy by scattering a quantum from the lattice, and changing its value (Raman process).

A measure of the time for the interaction to restore thermal equilibrium of the spin system with the lattice is the spin-lattice relaxation time \(\mathcal{T}_L\). For each of the two relaxation mechanisms in the case \(S = \frac{1}{2}\) Kronig estimated the relaxation times

\[
\mathcal{T}_L = C_i \frac{\Delta^4}{\lambda^2 H^4 T} \quad \text{(direct process)}
\]

\[
\mathcal{T}_L = C_i \frac{\Delta^6}{\lambda^2 H^6 T^6} \quad \text{(Raman process)}
\]

where \(\Delta\) is the energy difference in \(\text{cm}^{-1}\) between the ground state and the next orbital level above the ground state, \(\lambda\) is
the spin-orbit coupling coefficient, $T$, the lattice temperature and $c_t$ and $c_L$ constants to correct the dimensions. It has been found that the line width is inversely proportional to $\tau_L$ and in turn, that ions with small values of $\Delta$ have wide absorption lines. In practice the temperature is reduced until the line width is due to spin-spin and not spin-lattice interaction.

c. $\beta)$ Spin-Spin Interaction

The other broadening is due to the mutual interactions of magnetic dipoles. General theories for this interaction have been developed by van Vleck $^{11}$, and Pryce and Stevens $^{12}$ under the assumption that $\tau_L$ is long.

The magnetic dipoles which precess in the applied magnetic field, have a steady component in the direction of this field. This component will produce an extra field at the neighbouring ions which alters the total field slightly and hence shifts the energy levels. It can be shown that this effect varies with the applied magnetic field, and the contribution of each neighbouring dipole has an angular dependence of the form $(1 - 3 \cos^2 \theta)$, where $\theta$ is the angle between the dipoles and the applied field. The rotating component of the precession also causes a broadening as it interacts on other spins of the same Lamor frequency and induces transitions which decrease the lifetime of the energy state. If the two dipoles have different precessional frequencies, the rotating fields have little effect.

According to van Vleck the mean-square-width of a line
due to dipole-dipole interaction between free spins is proportional to
\[ \left( \frac{3 \mu_1^2 \Theta - 1}{r^3} \right)^2 \]
where \( \Theta \) is the angle between the axes of two magnetic moments \( \vec{\mu}_1 \) and \( \vec{\mu}_2 \), and \( r \) is the distance between \( \vec{\mu}_1 \) and \( \vec{\mu}_2 \).

It can be seen from the terms in \( r^6 \) that spin-spin interaction falls off rapidly with distance, and in calculating the line width it is usually only necessary to consider immediate neighbours. The spin-spin interaction is independent of the temperature and the strength of the magnetic field and can be reduced by diluting the salt with an isomorphous diamagnetic lattice. The line shapes cannot be made arbitrarily thin because of the interactions of nuclear magnetic moments of the neighbouring diamagnetic atoms with the spin system in question.

c. \( \gamma \) ) Exchange Interaction

When the paramagnetic ions are close enough together there is a great probability that an electron from one ion will be found in the other ion. If the ions are similar the effect of exchange is to narrow the lines at the centre, and broaden them in the wings, leaving \( (\Delta H)^2 \) unchanged, but reducing the width measured at half power points. If the dipoles are very close together so that the exchange energy is much larger than the dipole interaction energy the absorption is concentrated in the narrow peak which is called "exchange narrowing". If the exchange takes place between dissimilar ions the exchange
interaction will bring two different transitions together and hence produce a wider line.

A theoretical treatment of exchange interaction has been given by van Vleck \(^{11}\), and Pryce and Stevens \(^{12}\).

1.3) References

3) Elliott, R.J., Stevens, K.W.H., Phys. Soc. A64 (1951), 205
Bowers, K.K., Owen, J., Reports Progr. Phys. 16 (1953), 108
Van Vleck, J.H., The Theory of Electric and Magnetic Susceptibilities (1932 Oxford)
8) Bleaney, B., Phil. Mag. 42 (1951), 441
9) Kronig, R. De La, Physica 6 (1939), 33
10) Van Vleck, J.H., Phys. Rev. 57 (1940), 426
11) Van Vleck, J.H., Phys. Rev. 74 (1948), 1168
II) EXPERIMENTAL TECHNIQUE

In this chapter we will briefly describe details of the paramagnetic resonance technique as it has been used in this work.

2.1) The Experimental Method in Paramagnetic Resonance

The paramagnetic sample is placed into a radio frequency field of amplitude $\hat{H}$ and frequency $\nu$, at right angles to which there is a constant magnetic field $H_0$. If the resonance condition

$$h\nu = g\beta H_0$$  \hspace{1cm} (1)

is fulfilled, magnetic dipole transitions occur. These transitions are associated with power absorption from the microwave field. From a macroscopic viewpoint this absorption can be described by means of the imaginary part $\chi''$ of the complex paramagnetic susceptibility $\chi = \chi' - i\chi''$ of an assembly of magnetic dipoles as outlined in chapter I. The transmitted or reflected microwaves will also experience a phase shift which is associated with the real part $\chi'$, but we are not interested in the latter.

The resonance condition (1) can be satisfied at fields and frequencies as low as desired. However, the signal strength increases with frequency as explained in a later chapter.

Moreover, the line width of paramagnetic salts is usually of the order of 0.01 cm$^{-1}$ to 0.1 cm$^{-1}$. Hence, no resolved lines would be observed except at higher wave numbers. Further, in many
paramagnetic salts the initial splitting of the ground state is of the order of 0.1 cm\(^{-1}\) to 1 cm\(^{-1}\). Then transitions can only be induced at frequencies with wave numbers \(\tilde{\nu}\) higher than these splittings. It is therefore advantageous to work at frequencies as high as possible. The upper limit is set by the fact that microwave techniques have been developed only up to 60 kMc/s and that magnets giving fields over 1.6 \(\cdot\) 10\(^5\) A/m (\(\approx\) 20 kOe) are too expensive.

In the majority of known paramagnetic salts the splittings of the ground states are smaller than 0.3 cm\(^{-1}\). Hence, paramagnetic resonances can be observed in the 3 cm band. When this work was started the only available magnet was one which reaches at most 5.2 \(\cdot\) 10\(^5\) A/m (\(\approx\) 6 kOe) with a 2 inch gap. A 2 inch gap is the minimum space required for a 3 cm cavity resonator surrounded by two dewars. Hence, the 3 cm band was chosen.

Most of the research in paramagnetic resonances is carried out at low and sometimes very low temperatures because of the increase of susceptibility with decreasing temperature and because of relaxation processes which broaden the resonance signals at higher temperatures.

The temperature at which the sample can be investigated depends on the relaxation times of the magnetic dipoles under consideration. The best signals are obtained when the relaxation time \(\tau_2\) is long enough to permit the absorption of energy but not so long as to cause saturation. This relaxation time is usually of the order of 10\(^{-5}\) to 10\(^{-7}\) seconds and can be obtained
at room or liquid air temperatures for salts containing ions of the iron group, whereas the rare earth group ions (except gadolinium) require liquid hydrogen or liquid helium temperatures. Therefore, this spectrometer was built for operation at all temperatures between $1.3^\circ K$ and room temperature.

In paramagnetic resonance absorption the usual practice is to set the microwave oscillator at a fixed frequency and sweep the absorption line through this frequency by varying the magnetic field $H = H_o + H_s \cos \omega t$ of which the amplitude $H_s$ of the sinusoidal sweep is large compared with the line width of an absorption line.

To obtain a measurable absorption in a small volume of sample the energy density of the microwave radiation is increased by putting the sample in a high $Q$ resonant cavity. The sample will be placed in that part of the cavity where the magnetic part of the microwave field is maximum. The power absorption in the paramagnetic system of the sample reduces the $Q$ of the cavity resonator and hence the transmitted power to the detection system, where the resonance signal will appear as a dip in the microwave carrier (amplitude modulation).

Measurements of the microwave frequency, the magnetic field, and the temperature give the experimental data for the description of the resonance spectrum of a paramagnetic salt.

2.2) Choice and Preparation of Samples

The choice of the sample depends, of course, on the
details of the problem. If a paramagnetic ion in a particular lattice is to be studied then the choice of the sample is governed by the following requirements:

1) Single crystals must grow easily in a desirable shape (in general one with a low surface to volume ratio).

2) The crystal must withstand a wide range of temperatures (in many cases low temperatures are desired) without cracking and be chemically stable.

3) When the crystal has to be used in an evacuated cavity it has, of course, to withstand vacuum.

4) Some crystals are hygroscopic and have to be covered with a thin film of varnish.

5) There should be only one paramagnetic ion in a unit cell or, if there are more, they should be magnetically equivalent with respect to the surrounding diamagnetic atoms. This makes it easier to mount the crystal in the proper place and gives maximum intensity in the spectrum.

It is advantageous to know the crystal structure from x-ray analysis in order to simplify the determination of the form of the potential function which must be consistent with the crystal symmetry.

As in many problems in paramagnetic resonances the dipole-dipole interaction is not wanted, because of the line broadening. In order to reduce the line width mixed crystals are grown in which some of the diamagnetic ions are replaced by paramagnetic ions according to the wanted "dilution" of the
magnetism. Then the crystal structure should be isomorphous throughout the diamagnetic and paramagnetic ions, and the radii of the ions concerned should not differ too much.

The limiting line width in a hydrated crystal is due to the fluctuating magnetic field of the protons in the neighbouring water molecules of crystallization. The limiting half-power line width due to this field is about 480 A/m (≈ 6 Oe) for hydrated salts. This line width, however, can be reduced to about 160 A/m (≈ 2 Oe) by growing crystals from heavy water.

To obtain maximum signal strength, the samples should also have a certain size which depends on the geometrical distribution of the magnetic field in the cavity resonator (see section 2.3) d). The samples should be reliably fixed in situ in the cavity.

In this work the samples were attached with silk threads and glue to tiny teflon supports which were screwed into the crystal holder. The crystal holder was made to serve as a microwave circuit element (choke plunger) which prevents microwave frequency radiation from the cavity going up the German silver tubing (for further details see section 3.2).

The choke plunger offers sufficient room to attach an additional test sample with a known number of spins and known splitting factor. Usually the sample to be investigated and the test sample are run simultaneously. The test sample can be, for instance,
a) D.P.P.H. (diphenyl-trinitro-phenyl-hydracyl) \((C_6H_5)_2N - NC_6H_2(NO_2)_3\) hermetically sealed in a small cube of teflon. The number of spins can be controlled by dissolving a known amount of D.P.P.H. in benzene and weighing. The splitting factor is \(g = 2.0036 \pm 0.0002\), and the line width is \(\approx 108\; \text{A/m} \quad (\approx 1.35 \; \text{Oe})\).

or

b) \(M_{n^{++}}\) diluted in \(Zn(NH_4)_2(SO_4)_2\cdot6H_2O\), the spectrum shows 41 hyperfine structure lines.

2.3) Theory of the Spectrometer

The considerations given in this chapter have been found very useful in designing paramagnetic resonance experiments. They have been derived from references in Montgomery \(^1\), and Feher \(^2\).

a) Change of \(Q\) of the Cavity Resonator

Let us consider a sample, a paramagnetic crystal, of which any dimension \(d\) is small in comparison with half of the wave length, \(\frac{\lambda}{2}\), inside the cavity resonator. The sample has electric and magnetic susceptibility. The power absorbed in a paramagnetic crystal is

\[
P_s = \frac{\omega}{2} \int \chi'' \frac{\hat{H}}{V_s} dV_s + \frac{\omega}{2} \int \chi'' \frac{\hat{E}}{V_s} dV_s
\]

where \(\chi''_m\) and \(\chi''_e\) are the imaginary parts of the radio frequency magnetic and electric susceptibility respectively, and \(V_s\) the volume of the sample. For sufficiently low powers \(\chi''_m\) and \(\chi''_e\) are not functions of \(\hat{H}\) and \(\hat{E}\) respectively. The \(Q\) of a cavity
resonator in which a paramagnetic sample is placed is given by

\[ Q = \omega \frac{\text{peak energy stored in cavity}}{\text{average power dissipated}} = \omega \frac{\sqrt{\frac{1}{2} \int \mathcal{H}^2 dV_c}}{P_L + \frac{\omega}{2} \int \{ \epsilon_s \mathcal{H}^2 \mathcal{X}_{\mathcal{M}} + \epsilon_e \mathcal{E}^2 \mathcal{X}_{\mathcal{E}} \} dV_s} \]

where \( P_L \) = power loss in the walls of the cavity, depending on resistivity of the metal and the skin-depth, \( P_s \) = power loss in the sample, \( V_c \) = volume of the cavity, \( V_s \) = volume of the sample. For the time being we shall omit the power loss due to radiation or coupling.

Rearrangement of equation (3) gives

\[ Q = \omega \frac{\int \mathcal{H}^2 dV_c}{P_L + \frac{\omega}{2} \int \{ \epsilon_s \mathcal{H}^2 \mathcal{X}_{\mathcal{M}} + \epsilon_e \mathcal{E}^2 \mathcal{X}_{\mathcal{E}} \} dV_s} \]

Here the factor \( \frac{\omega}{2} \int \frac{\mathcal{H}^2}{V_c} dV_c \) is the unloaded \( Q_o \). Assuming that the paramagnetic and dielectric losses are small in comparison with the power loss in the walls, \( P_L \), we obtain

\[ Q = Q_o \left[ 1 - \frac{1}{\frac{P_L}{2}} \frac{\omega}{2} \int \{ \epsilon_s \mathcal{H}^2 \mathcal{X}_{\mathcal{M}} + \epsilon_e \mathcal{E}^2 \mathcal{X}_{\mathcal{E}} \} dV_s \right] \]

\[ = Q_o \left[ 1 - \frac{\omega}{2} \mathcal{X}_{\mathcal{M}}^{\text{m}} Q_o \frac{\int \mathcal{H}^2 dV_s}{\int \mathcal{H}^2 dV_c} - \frac{\omega}{2} \mathcal{X}_{\mathcal{E}}^{\text{m}} Q_o \frac{\int \mathcal{E}^2 dV_s}{\int \mathcal{E}^2 dV_c} \right] \]

and

\[ \Delta Q = Q_o - Q = Q_o \left[ \mathcal{X}_{\mathcal{M}}^{\text{m}} \eta_H + \mathcal{X}_{\mathcal{E}}^{\text{m}} \eta_E \right] \]

is the entire change of \( Q \) due to the presence of the sample.
The factors
\[
\begin{align*}
\eta_H &= \frac{\int_V \left\{ \frac{H^2}{E^2} \right\} dV}{\int_V \left\{ \frac{H^2}{E^2} \right\} dV_c} \\
\eta_E &= \frac{\int_V \left\{ \frac{H^2}{E^2} \right\} dV_s}{\int_V \left\{ \frac{H^2}{E^2} \right\} dV_c}
\end{align*}
\]
(5)

are the filling factors which depend on the field distribution in the cavity and the sample. For example, in a rectangular cavity excited in the TE_{101} mode (a modified shape of this has been used by the author as described later)

\[\eta_H = \frac{2V_s}{V_c}\]

Here it is assumed that \(\hat{H}^2\) does not vary over the volume of the sample. The relative change of \(Q\) due to the presence of the sample is

\[\frac{\Delta \omega}{Q_o} = Q_o \left\{ \chi''_H \eta_H + \chi''_E \eta_E \right\}\]

(6)

The left term on the right side in equation (6) determines essentially the strength of the signal, since the dielectric losses are kept negligible by placing the sample in that part of the cavity, where the magnetic component of the microwave field has its maximum and the electric field is almost zero over a small range. The unloaded \(Q_o\) mentioned above is already affected by the input and output coupling.

These couplings essentially couple a load into the cavity, and an additional load then comes from the sample as it has been considered here. Although there is physically no difference between a loaded and a coupled cavity I like to distinguish between those in the formulas. In the following we
shall distinguish clearly between the unloaded uncoupled $Q_0$, the unloaded coupled $Q_{oc}$, and the loaded coupled $Q_L$.

b) Equivalent Circuit of a Transmission Cavity and Optimum Coupling

In order to draw an equivalent circuit diagram, the following simplifications are made: All the losses inside the cavity shall be represented by the resistance $R$, the couplings by means of mutual inductances, and the generator and load impedance are equal to the characteristic impedance of the transmission line $R_0$. Then the following figures show an equivalent circuit for a transmission cavity.

Let us assume that $\omega l_1 \ll R_0$, $\omega l_2 \ll R_0$, then seen from the cavity the circuit diagram takes the form

The power delivered to the load in case of resonance is

(7)
The coupled $Q_{oc}$ of the cavity is

$$Q_{oc} = \frac{\omega_0 L}{R + \frac{(\omega_0 M_1)^2}{R_o} + \frac{(\omega_0 M_2)^2}{R_o}} = Q_o \frac{1}{1 + \frac{(\omega_0 M_1)^2}{R R_o} + \frac{(\omega_0 M_2)^2}{R R_o}}$$

We obtain the uncoupled $Q_o$ of the isolated cavity by putting $M_1 = M_2 = 0$ or $R_o = \infty$. If we define the input and output coupling parameter

$$\frac{(\omega_0 M_1)^2}{R R_o} = \beta_1, \quad \frac{(\omega_0 M_2)^2}{R R_o} = \beta_2$$

then $Q = Q_{oc} (1 + \beta_1 + \beta_2)$ and $P_L = \frac{\beta_1 \beta_2 E^2}{R(1 + \beta_1 + \beta_2)^2}$ (8)

Finally, the loaded and coupled $Q_L$ is defined by

$$\frac{1}{Q_L} = \frac{1}{Q_{oc}} + \frac{1}{Q_o}$$

where $\frac{1}{Q_o}$ represents the losses in the sample and may be given by

$$\frac{1}{Q_o} = \alpha P_o$$

where $\alpha$ is a proportionality factor making $\frac{1}{Q_o}$ dimensionless. $\frac{1}{Q_o}$ is numerically equal to

$$\chi'' \eta'' + \chi'' \eta''' \mu \nu \ell \epsilon$$

compare equation (4).

As already pointed out before the magnetic absorption in the cavity is equivalent to a change of the resistive load $R$. According to equation (7) a change of $R$ causes a change of the transmitted power to the load resistor. As far as the amplification of detected signals is concerned only the absolute power change
on the detecting load matters, assuming for the time being that
the signal to noise ratio does not depend on the power level on
the detecting load. In order to obtain a maximum power change
for a change in the resistive load we consider

\[ \Delta P_L = \frac{\partial P_L}{\partial R} \Delta R = -2 \frac{(\omega_0 M_1)^2 (\omega_0 M_2)^2 E_g^2}{R_o \left[ \frac{R}{R_o} + \frac{(\omega_0 M_1)^2}{R_o} + \frac{(\omega_0 M_2)^2}{R_o} \right]^3} \]

\[ = -2 \frac{\beta_1 \beta_2 E_g^2}{R_o (1 + \beta_1 + \beta_2)^3} \cdot \frac{\Delta R}{R} \]  \hspace{1cm} (10)

Then from \( \frac{\partial (\Delta P_L)}{\partial \beta_1} = 0 \), and \( \frac{\partial (\Delta P_L)}{\partial \beta_2} = 0 \) we obtain the
condition \( \beta_1 = \beta_2 = 1 \) for the optimum coupling. In this case
\( Q_{oc} = \frac{1}{3} Q_o \). When \( \beta_2 = 0 \) then \( Q_{oc} = \frac{1}{2} Q_o \), \( \beta_1 = 1 \) is the
condition that all the microwave power from the transmission line
is coupled into the cavity and dissipated there which case is
wanted for paramagnetic resonance saturation experiments.

c) Sensitivity of the Overall System

Before considering the sensitivity of the overall system some relations which are used in this section are given here.

From formula (8) and (10) the fractional change of power is

\[ \frac{\Delta P}{P_L} = - \frac{2}{3} \frac{\Delta R}{R} \]  \hspace{1cm} (11a)

or using the expression for the maximum power \( P_g \) available from
the klystron

\[ \frac{E_g^2}{4 R_o} \]
\[ \frac{\Delta P_L}{P_g} = - \frac{8}{27} \frac{\Delta R}{R} \]  

which gives the transmission loss ratio

\[ \frac{P_L}{P_g} = \frac{4}{9} \]  

(12)

From equation (4) follows that the relative change of \( \mathcal{Q} \) is \( \frac{\Delta \mathcal{Q}}{\mathcal{Q}_{oc}} = \mathcal{Q}_{oc} \mathcal{X}_m'' \eta_H \) neglecting \( \eta_E \). The magnetic absorption in the cavity is equivalent to a change in the series resistive load. Hence,

\[ \frac{\Delta \mathcal{Q}}{\mathcal{Q}_{oc}} = - \frac{\Delta R}{R} \]  

(13)

and

\[ \mathcal{Q}_{oc} \mathcal{X}_m'' \eta_H \frac{2}{3} \frac{\Delta P_L}{P_L} = \frac{2 \cdot \Delta E_L}{\sqrt{P_L R_o}} \]

The smallest detectable voltage change \( \Delta E_L \) is assumed to be equal to the noise voltage \( \mathcal{E}_N \) generated by the receiving system.

\[ \Delta E_L = \frac{\sqrt{P_L R_o}}{3} \mathcal{Q}_{oc} \mathcal{X}_m'' \eta_H = \mathcal{E}_N \]  

(14)

The microwave crystal diode is terminated by an video amplifier. Assuming that the internal impedance of the used amplifier is equal to that of the detecting crystal diode, namely \( R_o \), and that both systems are at the same temperature \( T \), have an overall bandwidth \( \Delta \nu \) and noise factor \( F \), we find

\[ \mathcal{E}_N = \sqrt{2 \kappa T \Delta \nu R_o F} \]  

(15)

Thus the minimum detectable radio frequency susceptibility is

\[ \mathcal{X}_m''(\nu) \geq \frac{3}{\mathcal{Q}_{oc} \eta_H} \sqrt{\frac{2 \kappa T \Delta \nu R_o F}{2 P_g}} = \frac{9}{\mathcal{Q}_{oc} \eta_H} \sqrt{\frac{\kappa T \Delta \nu R_o F}{2 P_g}} \]  

(16)
The radio frequency susceptibility $\chi''(\nu)$ is given by

$$
\chi''(\nu) = \frac{\bar{G}}{G_0} \frac{\beta^2 \gamma^2 \nu^2}{\beta \kappa T} \left( \frac{\gamma (s+1) - M(M-1)}{2s+1} \right)
$$

(17)

where $f(\nu)$ is the normalised line shape function according to Bloembergen, $N_p$ is the number of paramagnetic ions per unit volume, $\beta$ Bohr's magneton, $\gamma$ the splitting factor, $\kappa$ Boltzmann's constant, $T$ the absolute temperature.

From this formula the minimum detectable number $N$ of paramagnetic ions can be calculated. On the other hand, when a signal of a test sample having a known $N$ and $\gamma_H$, can just be distinguished from noise, the noise figure of the receiving system can be calculated.

From formula (16) follows that the signal strength is proportional to the unloaded $Q_{oc}$ of the cavity, to the filling factor $\gamma_H$ of the sample, and to the square root of the power input to the cavity.

An increase of the power input helps only to a certain extent. For each microwave diode such as the 1N23B which was used for detection in this work there exists an optimum power level for which a maximum signal to noise ratio is obtained. This power level is about 1 mW and is obtained when the rectified current is about 500 $\mu$A.

The susceptibility increases with frequency, and formula (14) tells us that the sensitivity increases with the frequency of resonance.
d) Optimum Size of the Sample

We have seen that the signal strength is proportional to the magnetic filling factor. A large sample volume, however, immerses too much into that part of the cavity in which the electric field is high, and the loaded $Q_L$ decreases proportional to the dielectric filling factor. An optimum size for a sample also exists.

Let us consider a sample which is placed at one end of a rectangular cavity resonating in the $TE_{101}$ mode. There the magnetic component of the microwave field is strongest, and when the sample is small in comparison with $\frac{\lambda}{2} = \alpha$ of the cavity, the magnetic component is to a first approximation constant over the volume of the sample. If the sample extends a small distance $z$ in the direction of increasing electric field then the dielectric loss is proportional to

$$\chi'' \hat{E}^2 \int_0^\frac{\pi}{\alpha} \sin \left(\frac{\pi}{\alpha} z\right) dz \approx C \cdot z^3$$

where $C$ is a constant. The dielectric loss rises with $z^3$. The volume of the sample $V_s$ is proportional to $z$ and the magnetic losses are approximately proportional to $z$. Then the total $Q_L$ is given by

$$Q_L = \frac{1}{\frac{1}{Q_c} + \alpha z^3}$$

Where $\alpha$ is a constant making $\alpha z^3$ equal to $\frac{1}{Q_s}$ which was defined in formula (9). Since the volume $V_s$ of the sample is proportional to $z$ then
The detected voltage change $\Delta E_L$ is proportional to this expression. Maximizing this expression with respect to the length $z$, results in

$$\alpha \frac{z^3}{Q_{oc}} = \frac{1}{2 Q_{oc}}$$

and hence

$$Q_L = \frac{1}{Q_{oc}} + \frac{1}{2 Q_{oc}} = \frac{z}{3} Q_{oc}$$

A maximum signal is therefore obtained when the cavity is loaded such that the unloaded $Q_{oc}$ is reduced by a third of its value.

2.4) References

1) Bleaney, B., Stevens, K.W.H., Reports Progr. Phys. 16 (1953), 108

2) Montgomery, C.G., Technique of Microwave Measurements, Radiation Laboratory Series 11

3) Feher, G., Bell System Techn. Journ. 36 (1957), 449
III) THE 3 cm PARAMAGNETIC RESONANCE SPECTROMETER

3.1) The Microwave Source

A paramagnetic resonance spectrometer requires a radiation source which

a) generates a single microwave frequency of sufficient power,

b) can be tuned over a certain frequency range, say about 10%,

c) Possesses a long time frequency and power stability

d) generates very little noise.

A satisfactory microwave source for the 3 cm band is the 723 A/B klystron, which gives under optimal matching conditions about 20 mW power output.

A high stability, low ripple power supply was essential to satisfy the above-mentioned requirements. For the 723 A/B an electronically regulated power supply was designed from a standard circuit found in Elmore & Sands. The power supply delivers the required beam voltage +300 V d.c., a beam current of 22 mA, and has a wide range of reflector voltage from -150 V to -270 V d.c. Fig. 1 shows the circuit diagram. The stabilisation factor obtained was $10^2$ for the beam voltage, and the ripple was about 1 mV. For the reflector supply a battery was chosen and, to obtain a long time stability for the reflector potential, the battery current was kept below 0.1 mA. A small microammeter indicated the battery current. This arrangement worked
Figure 1

Stabilized Klystron Power Supply
for the 723 A B Klystron
satisfactorily. A voltage drop during a run was not noticed. The filament voltage of the klystron was supplied by a 6 V storage cell, instead of an a.c. source, in order to avoid 60 c/s frequency modulation. A vacuum diode inserted between the reflector and the cathode of the klystron, prevented this element from becoming positive with respect to the cathode and destroying the tube because of excess beam current and secondary emission from the reflector. A fuse in the cathode lead also limits the cathode current. To facilitate finding the resonance frequency of the cavity provision was made to modulate the klystron reflector at audio frequencies using a sine or a square wave audio frequency generator. For details see the diagrams. The frequency generated by the 723 A/B is very sensitive to the temperature of the tube shell. It was found that the frequency stability was fair (the drift was about 1 Mc/s over half an hour) when the klystron tube was protected by a cylindrical metal screen against draft of air in the room.

For many investigations in paramagnetic resonances it is advantageous to have a higher power level available because of the following reasons:

a) The signal strength increases with the square root of the power (provided that the electron spin-lattice relaxation time is short enough to prevent saturation).

b) In some experiments such as the influence of the paramagnetic resonance saturation on the paramagnetic Faraday effect or the Overhauser effect a high microwave frequency
HIGH VOLTAGE STABILIZED KLYSTRON POWER SUPPLY

FIGURE 2

SINUSOIDAL or SQUAREWAVE AUDIO FREQUENCY GENERATOR

KLYSTRON BOX
Power level is wanted.

c) An optimum of the input and output coupling can always be achieved regardless of the available power level which will always be sufficient.

d) The optimum power level on the detecting crystal diode can always be obtained.

Therefore, a high power and high voltage klystron 2K39 was bought and the stabilized power supply designed from a standard circuit found in Elmore and Sands.

The difficulty in designing and constructing was to obtain the fairly high beam current of about 50 mA at a constant output voltage of about 1200 V. The circuit shown in the figure is very stable. The following measured quantities did not vary noticeably over 8 hours:

- beam voltage 1050 V,
- beam ripple smaller than 1 mV,
- beam current 50 mA.

For a 20% change of the input voltage (the variac in front of the high voltage supply has been used) the beam voltage varies about 0.5%. This gives a stabilization factor of about 100.

The line supply voltage feeding all the electronic equipment including the klystron power supply was stabilized by a constant voltage transformer (Sola) having a stabilization factor of 20.

The instability of the reflector voltage full value of which is -700 V with respect to the cathode did not exceed
1 V for a 20% change of input voltage. This is good enough, since 1 V change causes a deviation of 0.35 Mc/s only. The ripple of the reflector voltage is smaller than 1 mV.

The 2K39 klystron was operated in a bath of transformer oil, the oil being cooled by tap water. This way any thermal drift of frequency was prevented, and the frequency could be kept constant over 8 hours. Deviations were not noticeable (hence frequency deviation < 1 Mc/s).

3.2) The Cavity Resonator

It is a good investment for a paramagnetic resonance spectrometer to build a high Q cavity resonator. When neglecting the importance of the detecting system, most of the sensitivity depends on the Q of the cavity. In experiments employing power saturation of the magnetic spin system a high Q cavity resonator is essential.

The fact that a high Q cavity resonator makes the spectrometer very sensitive to microphonics demands, however, that the centre conductor in the coaxial transmission lines which feed microwave power into and out of the cavity is fairly rigidly supported and that no part of the low temperature equipment touches the magnet which is shaken by the modulation. The klystron frequency was found to be so stable that a high Q was no disadvantage.

The idea was to make an essentially rectangular cavity resonator as the direction of polarisation is known very
FIGURE 3

GEOMETRY of the CAVITY

CROSS-SECTION of the CAVITY
accurately, and since the probability of transitions induced by magnetic dipole coupling varies with the angle between the d.c. and radio frequency fields. This cavity should consist of two halves and should have such a shape that each part can be machined on a mill entirely from one piece, and all soldering can be avoided (see picture).

A transmission type resonator was designed in form of a combined rectangular and cylindrical cavity (see picture) for operation at $\nu = 9300 \text{ Mc/s}$ in the $\text{TE}_{101}$ mode. In the calculation of the resonant frequency the area of the cross-section was substituted by an equivalent rectangular area having the same width but a modified length.

The cavity was divided into two halves where the magnetic field had a node. The upper part of the cavity was provided with holes for admission of two coaxial lines and the crystal holder, and further with two holes in the large faces to let light through as required for magneto-optical experiments. The bottom part was held by copper-bronze clamps. The cavity could be sealed vacuum tight with Wood's metal in a groove provided. The windows could be closed with Indium-glass-brass seals or simply by brass caps, when no light had to be transmitted. The two coaxial lines ended each in a half turn loop for coupling power into and out of the cavity. The couplings were adjusted to their optimum value, and were insulated from the cavity and held in position by teflon screws as shown in the picture.
FIGURE 4

The 3 cm RESONATOR

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For the mounting of the crystals to be investigated interchangeable holders had been built. The end of a holder was mounted in a hole of the cavity (see Fig. 4) such that both surfaces are flush with each other. The crystal holders were made to serve as a microwave circuit element (choke plunger) which prevents microwave frequency radiation going up the German silver tubing. When the sample had to be interchanged just another crystal holder to which a new sample was already attached had to be screwed into a connector provided. The crystal holders can be rotated from outside by means of a vacuum tight ground joint seal which cone is equipped with a vernier dial movable over a coarse dial. This arrangement allows to read the angle of orientation to 1° accuracy, and angles of $\frac{1^\circ}{2}$ can be estimated.

Into the choke plungers tiny teflon supports of different shape (as can be seen from Fig. 4) can be screwed to which the samples can be attached by means of silk threads and cement. By the way, any other form of attaching the samples as the use of glue, radio service cement etc. or plasticine is unreliable at low temperatures.

As a highly conductive material for building the cavity pure silver was considered. Several tests in the workshop, however, proved that chemically pure silver is too soft for machining. Silver alloys have not the desired high electrical conductivity. Therefore, it was decided to silver plate a brass cavity. This is more advantageous because electrolytically deposited silver is, when annealed, almost single crystalline,
and its electric conductivity is much higher than that of solid silver.

The walls of the cavity were treated in the following way:

1) They were mechanically polished.
2) Then they were slightly etched with diluted \( \text{H}_2\text{PO}_4 \) and copper-plated.
3) The copper was polished and slightly etched.
4) Then it was silver-plated with a low current density.
5) The silver was ball burnished and then
6) annealed at 200° C.
7) Finally it was electrolytically polished.

The details of this procedure are given in the appendix of this thesis.

The Q could not be determined accurately because of the sharp tuning of the whole microwave circuit. The Q was measured by varying the resonant frequency between half power points. For optimum coupling Q is about 6500 ± 10% at room temperature and with an optimum size sample, about 5000. At 4.2° K the loaded \( Q_L \) was about 9000 when the microwave transmission line was critically coupled to the cavity. At 1.4° K \( Q_L \) was probably much higher. This uncoupled and unloaded \( Q_o \) corresponding to \( Q_L \) 9000 would be of the order of 20,000.

3.3) The Transmission Line System

The transmission line system is shown in the block
BLOCK DIAGRAM

of the 3cm PARAMAGN. RESONANCE SPECTROMETER
diagram of the spectrometer (Fig. 5).

The microwave power from the klystron is fed into a waveguide via a coaxial lead into a fixed quarter wave transformer. The klystron is matched to the waveguide system by a variable susceptance consisting of a movable stub in a slot in the waveguide and two flap attenuators consisting of a movable thin bakelite sheet covered with carbon paper. The microwave power is monitored by a crystal diode in a tunable auxiliary guide which is coupled to the main guide by a Bethe-hole coupler. The auxiliary guide also contains the precision frequency meter PRD 529-B, a transmission type direct reading cavity wave-meter. It has a frequency range from 8.2 kMc/s to 10.0 kMc/s giving a reading accuracy of 1 part in $10^4$.

The waveguide system is of standard design. The parts have been made in the workshop from rectangular guides RG-52U. An adjustable quarter wave transformer couples the waveguide to a flexible coaxial Uniradio 32 cable. A small waveguide section consisting of an adjustable quarter wave transformer and a tunable crystal mount was used for detecting the transmitted microwave power from the cavity resonator.

The two coaxial cables were joint to the low temperature equipment by means of ultra-high frequency cable connectors and female adapters as can be seen from Fig. 6. The top ends of the coaxial guides of the low temperature equipment are cable connectors which were sealed with solder and pizein as shown in the picture. This arrangement makes an excellent vacuum seal
FIGURE 6

DETAILS of the COAXIAL LINES, VACUUM SEALS
and COUPLING to CAVITY

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although these joints are not at all reflectionless. Nevertheless, enough power was obtained for all investigations in this thesis.

For the coaxial guides German silver was used because of its low thermal conductivity.

The outer conductor of the coaxial guides consists of 4 mm German silver tubes whose top ends were soft soldered into bent copper tubes. The inner conductors are 1 mm German silver capillaries. The capillary is kept in place by thin polyethylene discs which sit in pairs $\frac{\lambda}{2}$ apart. They set very tight on the capillary and fairly tight on the outer conductor. Notches in the discs permit evacuation. The great length of the coaxial lines is susceptible to microphonics, which are mainly caused by boiling liquid air.

3.4) The Detecting and Amplifying System

The transmitted microwave power from the cavity is fed into a tunable crystal mount (a tunable waveguide section as shown in Fig. 5) containing a 1N23B silicon tungsten crystal rectifier. The crystal was specially selected for low noise temperature and low conversion loss. However, since it is sometimes required to work with low microwave power in order to avoid paramagnetic saturation, a MA408A crystal was provided to replace the 1N23B. The optimum microwave power levels at which either crystal generates a minimum noise are for the 1N23B about 1 mW, which is obtained with a short circuited rectified current of about 500 $\mu$A, and for the MA408A approximately 1 $\mu$W.
FIGURE 7

BIAS NETWORK

for the DETECTING CRYSTAL DIODES

MA 408 A
or
IN 23 B

+ 10 kΩ

- 80 kΩ

6 V

1.5 kΩ

10 kΩ

0-50 µA

TO AMPLIFIER
For optimum operation the MA408A requires a positive d.c. bias of 50 µA. The bias network allows the adjustment of the self bias for the 1N23B and supplies the d.c. bias for the MA408A as shown in Fig. 7. In general, the detecting crystal is not matched to the microwave power source, but the crystal mount is tuned so that an optimum power level is obtained.

A switch is incorporated in the bias network so that some of the rectified crystal current can be fed to a microammeter or a galvanometer in order to check the tuning of the klystron to the cavity.

A shielded coaxial cable feeds the converted signal into a 2 stage amplifier. When the signal is observed on the screen of the cathode ray scope the 10 kΩ bias resistor is varied until the signal to noise ratio of the amplified signal does not improve any more. A matching between the input stage of the amplifier to the crystal converter is not important, since the overall noise figure of the receiving system is mainly determined by the crystal converter. The amplifier responds with low distortion from 60 c/s to 15 kc/s for signal input voltages from 10 µV to 2 mV and has a gain of 10,000. Though the amplifier has not been built for great sensitivity - since the converted crystal noise is dominant with this type of detection - precautions have been taken to protect it against microphonics and hum. Low microphony, low hum pentodes were chosen, and the stages of amplification mounted against shocks. The filaments of the tubes of both stages are supplied from a
FIGURE 8

VIDEO AMPLIFIER
d.c. battery. The plate supply voltages are obtained from an electronically stabilized power pack which was designed from a standard circuit given in Elmore and Sands.\(^1\)

The amplifier output is fed either directly or via a high pass filter to a Cossor type 1049 cathode ray oscilloscope with additional amplification. The filter which is a simple resistance capacitance network with an attenuation of 18db per octave below 175 c/s, was sometimes used to attenuate low frequency microphonics caused by boiling liquid nitrogen or liquid helium.

3.5) Production and Measurement of the Magnetic Field

a) The Electromagnet

A small general purpose electromagnet was available which generates a field of \(480.10^3 \text{ A/m} \approx 6 \text{ kOe}\) across a 2 inch gap. A gap of 2 inches offers just enough space for a 3 cm wavelength cavity resonator inside the two dewars required for work at liquid helium temperatures.

The magnet is a U-shaped yoke with the magnetizing coils mounted on the pole pieces between the side arms. The pole pieces are cylindrical and of 10 cm diameter. The centre of each pole piece contains a cylindrical hole filled by a removable cylindrical rod whose end is flush with the surface of the pole such that no inhomogeneities are produced. When the rods have been removed, magneto-optical effects can be studied by sending light through the hollow poles in the direction of the magnetic
FIGURE 9

CURRENT CONTROL for the ELECTROMAGNET

FIGURE 10

MAGNETIC FIELD MODULATION CIRCUIT

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The pole pieces are also provided with shims to produce the homogeneous field required for proton resonances which provide accurate magnetic field measurements. The inhomogeneity of the field is roughly 0.1% over a volume of 1 cm³ in the centre at a 2 inch gap. For easy adjustment of the gap one side arm of the yoke and both poles can be moved.

The magnetizing coils are cooled by running water. They are connected in parallel and supplied by a 110 V d.c. generator. With a power input of 2.5 kW a field of $480 \cdot 10^3$ A/m ($\approx 6$ kOe) is obtained across a 2.15 inch gap. The same power input produces only $750 \cdot 10^3$ A/m ($\approx 9.4$ kOe) at a 1 inch spacing.

Since the generator output voltage could not be varied, the magnet current was controlled by water-cooled rheostats as shown in Fig. 9. The water cooling of both the coils and the rheostats was adequate since no drift of the field due to warming up of the magnet coils or of the rheostats was noticed when a paramagnetic resonance signal was observed. As protection for the magnet coils against unpredicted circuit breaks a Thyrite by-pass is incorporated in the control panel.

b) Magnetic Field Measurements

Two meters covering the ranges 0 - 20 A and 0 - 50 A for the magnet current are provided. The current readings on these instruments were calibrated by means of proton resonance. Since the magnetization curve of the magnet has a hysteresis,
calibrations were taken all along the hysteresis loop. Field measurements using this calibration were taken only when the field was increased from its lowest value or when decreased from an upper well-defined value of the hysteresis loop. The magnetic fields are reproducible with respect to this calibration to better than 0.3%, and their accuracy only depends on the meter deflections and their readings. This is more than adequate because most paramagnetic resonance lines are fairly broad.

As mentioned above, proton resonance is used to measure the magnetic field. The resonance principle is well known, and the application of nuclear magnetic resonance to the measurement of magnetic fields is nowadays a standard technique. We shall therefore not elaborate the theory. The resonance condition is $\omega = \gamma H$, where $\nu$ is the applied frequency, $\gamma$ the nuclear gyromagnetic ratio and $H$ the applied field.

For protons this becomes $H = \frac{0.23487}{4\gamma} \cdot \nu$, where $H$ is given in $A/m$ and $\nu$ in $s^{-1}$. $\gamma$ has been measured to an absolute accuracy of about 1 part in $4 \cdot 10^4$. To determine the magnetic field by this method the frequency at magnetic resonance is measured, and the accuracy in this determination can easily reach 1 part in $10^5$. For a precise determination of the magnetic field at the centre of a paramagnetic resonance signal both the proton resonance and the paramagnetic resonance signal are displayed simultaneously on the screen of the double beam oscilloscope using the same sinusoidal sweep of the magnetic field modulation, and the accuracy of this determination is
actually limited by the precision with which the proton resonance signal can be superimposed on or compared with the paramagnetic resonance signal. This limit is about 40 A/m ($\approx \frac{1}{2}$ 0e).

For accurate field measurements it is desirable to place the proton sample as close as possible to the paramagnetic crystal under investigation. At liquid helium temperatures solid proton samples have to be used which give fairly broad signals (about 800 A/m ($\approx 10$ 0e). The electric equipment involved to place a proton sample inside the choke plunger of the cavity or close to it is not simple because of the wide tuning range of the sample coil, since the field range for the study of paramagnetic resonances is fairly great. It is more convenient to handle interchangeable probes to be placed outside the dewars and close to them in the centre axis of the magnetic field. The field measurements can then be corrected with very little loss of accuracy.

Such an arrangement, a complete proton resonance machine for measuring magnetic fields, was already available. It consists of an oscillator, a detector, and a war surplus BC-221-AH frequency meter, which gives a continuous reading accuracy of 1 part in $10^4$. The proton resonance machine has a tuning head and four plug-in probes to cover the frequency range from 6.6 Mc/s to 38 Mc/s. Magnetic field determinations can be made in small regions of the gap space because the probes are made small as the samples are not larger than $\frac{3}{8}''x\frac{3}{16}''x\frac{3}{16}''$.

The field gradient in the direction of the centre field
axis near the centre of the gap was found to be about 400 A/m ($\approx 5$ Oe) per cm at a field of $160 \cdot 10^3$ A/m ($\approx 2000$ Oe). This is tolerable with respect to the line width of common paramagnetic resonance signals which are usually much larger than 800 A/m ($\approx 10$ Oe). Since the field gradient varies with the total magnetic field, it was determined for different fields in order to make appropriate corrections for the field determination of paramagnetic resonance signals.

3.6) Magnetic Field Modulation

For displaying the absorption signal the magnetic field is modulated either at 60 c/s or at 400 c/s using a sinusoidal sweep of an amplitude which is small as compared with the total magnetic field and large as compared with the line width of the paramagnetic absorption signal. The total sweep is usually not made larger than ten times the line width. When the sweep is about 20 times the line width the signal appears distorted because of the finite bandwidth of the video amplifier.

A pair of coils producing the modulation field are fitted on the pole pieces and clamped rigidly to the inside of the main coils. For detection of broad lines it is necessary to use a sweep of high amplitude. At a current of 7 A a.c. rms. the magnetic sweep from peak to peak is $40 \cdot 10^3$ A/m (or 500 Oe). In order to maintain this sweep over a longer period the coils which are enclosed in bakelite housings are cooled with
compressed air. Provision is made to cool them with running water. The layers of turns are widely spaced in spiral forms so that each layer has good cooling contact with the streaming air on both sides. They are varnished to stop vibration. Each coil is wound with 267 turns of No. 20 insulated copper wire. The supply and control of the magnetizing current is shown in Fig. 10.

The amplitude of the modulation is obtained by calibrating the readings of the current in the coils against the induced voltage in a search coil which is placed in the centre of the gap. This calibration was later checked with proton resonance absorption. The calibration was used for measurements of line widths.

The time base of the oscilloscope was taken from the same sinusoidal supply, but was independent of the amplitude of the modulation as shown in Fig. 10.

At high field and high modulation fields the vibration of the modulation coils was extremely noisy, although precautions were taken to avoid this as mentioned above. When any part of the apparatus touched the pole pieces the reception of signals was perturbed by strong microphonics. It was therefore carefully avoided that the dewars touched any part of the magnet.

3.7) The Low Temperature Apparatus

Experimental techniques at low temperatures are well known. In this section only details of the low temperature apparatus relevant to the particular problems are given.
The apparatus for paramagnetic resonances has two vacuum systems: a system to evacuate the cavity resonator, and a large capacity system to reduce the vapour pressure of liquid helium to obtain temperatures below 4.2°K. Fig. 11 illustrates the two vacuum systems.

All connections to the apparatus inside the inner dewar are made of thin German silver tubing because of their low thermal conductivity.

Much attention has been paid to obtain a good vacuum in the cavity, since condensation of gases and water vapour detunes the cavity and reduces its Q, and the crystal holder cannot be rotated when frozen to the tubing. In this respect a slight leak which is not noticeable at room temperature can become very troublesome at low temperatures. Therefore, the cavity was protected against these effects by both evacuation and refilling with clean helium gas to about one atmosphere pressure. A charcoal cleaner and trap was incorporated in the vacuum system as can be seen in the figure. When the system is cooled down to 4°K more helium gas is let into the cavity vacuum system to maintain a pressure which is a little below one atmosphere. A path to the return line is provided for the equalization of pressures when the system warms up. To check the vacuum and help in detecting leaks a mercury manometer and a Pirani gauge are provided. The Pirani gauge is used to give an indication of the pressure down to about one micron of Hg.

The temperature in the cavity resonator is measured
by means of a constant volume gas thermometer which has been calibrated for the range between 77.3°K and 4.2°K. This thermometer consists of a small copper bulb of 2 cm$^3$ volume soldered to the cavity, a long capillary, and a manometer connected to a large volume of 30 cm$^3$. The disturbing volume of the capillary was only 0.06 cm$^3$. The manometer was calibrated using two temperatures $T = 77.3°K$ and $T = 4.2°K$ known. The relation between the scale divisions of the manometer and the temperature is given by

$$\frac{p}{p_0} = \frac{1}{V + \frac{V}{\nu + V} \frac{T_0}{T}}$$

where $T_0 = 273.17°K$ and $p_0 = 1$ atm, $\nu$ and $V$ are the small and the large volumes, respectively. Temperatures below 4.2°K were measured by means of the vapour pressure of liquid helium. The empirically determined $p - T$ relation in form of tables has been used to convert the pressure into temperature.

For the large capacity system over the liquid helium bath, a high speed rotary pump was available in a room adjacent to the laboratory and was linked to the apparatus by a 4 inch pipe. The pressure of the helium vapour is indicated on a mercury manometer and an oil manometer. The oil manometer is used for pressures lower than 40 mm Hg. The density of this oil (Apiezon oil B) at 22°C is 15.6 times smaller than that of mercury. At maximum pumping speed, a temperature of 1.35°K can be obtained. As a help in attaining this temperature some liquid nitrogen is kept in the cap which seals the inner dewar. The inner dewar
contains about 1.5 litre liquid helium.

The liquid helium is obtained from a Collins liquifier and is stored in a 25 litre liquid helium can which serves as transport vessel. The helium is transferred from the storage container by applying a small overpressure of helium gas in the container. Details of the transfer system follow from the figure. When the inner dewar has been precooled to liquid nitrogen temperature, the liquid helium which evaporates in cooling the dewar from 77°K to 4.2°K amounts to about 0.25 litre, and from 295°K to 4.2°K to about 0.4 litre.

To obtain temperatures between 4.2°K and 77°K use was made of the great heat capacity of charcoal that is saturated with absorbed liquid helium 4). A copper vessel containing about 10 g charcoal was soldered to the lower part of the cavity with Wood's metal (see picture on page 36). The container is open on top and has a small hole at the bottom to allow the surplus of liquid helium to drain out. The device was operated in the following way: A small quantity of liquid helium was transferred into the tail of the inner dewar until the charcoal container was just flooded, and after the surplus of liquid helium was removed with a heat lamp, helium was desorbed by low speed pumping controllable by a conical valve. The obtained temperature was measured with a gas thermometer. It was possible to hold a temperature of 25°K constant over ten minutes when about 50 mW microwave power was dissipated in the walls of the cavity and the modulation sweep
of the magnetic field was kept small. When a high magnetic field sweep was applied, the cavity warmed up fairly quickly due to the eddy currents generated in the brass of the cavity. The temperature was measured with the gas thermometer.

3.8) Experimental Procedure

An outline of a typical paramagnetic resonance experiment at a temperature below 4.2°K will be given here.

After the paramagnetic crystal to be investigated has been mounted on the crystal holder in the desired orientation with respect to the plunger axis, the angle between one crystal axis and the zero marker of the dial on the spectrometer top is measured to an accuracy of approximately ± 2°. The correct zero reading follows from the symmetry of the rotational spectrum as explained below.

After the cone at the end of the long German silver tubing of the crystal holder has been coated with stopcock grease to provide a tight seal with the ground joint, the cavity is evacuated and a liquid air trap is cooled to provide a condensation centre for remaining gases. The cavity is then refilled to about 1 atm pressure with clean helium gas streaming through the charcoal cleaner.

The klystron power supply is now switched on. In most cases the klystron is already tuned to approximately the resonance frequency of the cavity, the klystron being operated on a broad "mode" of its reflector voltage. In difficult cases
of tuning, the reflector voltage is modulated at 60 c/s and the rectified power from both the klystron monitor (see Fig. 5) and from the cavity is displayed on the double beam Cossor scope, and the klystron frequency changed until the resonance curve of the cavity appears.

Meanwhile, both the helium dewar and the outer dewar are precooled with liquid nitrogen. The cavity is slowly precooled with liquid nitrogen using a small dewar. When the refrigerant has stopped boiling the dewar is removed and quickly replaced by the empty and precooled helium dewar while both the cavity and the helium dewar are still wet with liquid nitrogen. The evaporation of nitrogen is so intense that no frost condenses in the dewar. The rubber sleeve (see Fig. 11) which has been wetted with glycerine is then pulled over the helium dewar to make a good vacuum seal, and the helium dewar evacuated. The outer dewar containing some liquid nitrogen is slowly pulled over the helium dewar. The magnet is now rolled in place so that the dewars are well centred in the gap. The centering is tested with especially made brass callipers. The liquid nitrogen cap and the outer dewar are then filled up with liquid nitrogen.

After evacuation the inner dewar and the vacuum system are filled with clean helium gas from a helium cylinder. When the helium gas inside the inner dewar has cooled down to about 77°K, as read from the gas thermometer, the liquid helium transfer can start. Details of the transfer technique used are described in the preceding section.
The klystron is kept in tune with the cavity all the time. When enough liquid helium has been syphoned over, the pressure on both sides of the syphon is equalized, the syphon removed, and the whole system closed vacuum tight against outside. In order to obtain a temperature lower than the boiling point of helium, the return line is closed and the helium vapour pumped off with a high speed rotary pump. The pumping speed can be adjusted and throttled by means of valves and the temperature obtained read off the vapour pressure manometer. Adjustments continue until the desired temperature has been obtained.

The magnet is then switched on and its field several times cycled along the hysteresis loop in order to accurately reproduce the calibration curve. Now the modulation field, the receiver, and the oscilloscope are switched on, and the magnetic field is slowly increased until a paramagnetic resonance signal appears.

Final adjustments are made to the various matching devices of the waveguide system until optimum transmission conditions are obtained. The tuning of the klystron to the cavity is then improved as long as the line seems to be distorted due to anomalous dispersion.

The power is also varied until an optimum signal to noise ratio is obtained. Further improvements are made by adjustments to the bias network. The modulation sweep is adjusted so that it is about 5 to 10 times the line width of the signal. By this time the klystron frequency and the
temperature in the inner dewar are so stable that they need no special care for the next couple of hours.

The orientation of the paramagnetic crystal in question is checked by rotating it until an extremum of the splitting is observed; then the crystal axis is either parallel or perpendicular to the magnetic field. Final corrections to the complete rotational spectrum using this fact can be made later when the experiment is finished. When the proton resonance machine is in operation, a proton resonance signal is simultaneously displayed on the scope. Then the extrema of the splittings relative to the proton signal can be found with great precision.

For a determination of the magnetic field the proton signal is brought into the centre of the paramagnetic resonance signal, and the proton resonance frequency is measured by the tuning of the standard oscillator of the frequency meter to give zero beat. If an error in the field determination of 0.3% is tolerable the ammeter readings are sufficient. The microwave frequency is measured with a calibrated wavemeter.

For any change in orientation of the crystal axis under investigation with respect to the magnetic field axis the klystron requires a slight retuning because of the high Q and the change in load of the cavity due to change of susceptibility.

As another example, the experimental procedure of an investigation of the Faraday effect shall be outlined here.

The experimental set-up for the Faraday effect will be described in details in chapter VI, and the reader is asked
to look at this chapter first. To increase the Faraday rotation the experiments were all carried out below the \( \lambda \)-point (2.19°K). In this case the cavity need not be sealed as the superfluid helium prevents boiling of liquid helium in the cavity in spite of the great amount of power dissipated in the walls of the cavity. Since the crystal under investigation \( \text{Nd(C}_2\text{H}_5\text{SO}_4)_3\cdot 9\text{H}_2\text{O} \) cannot stand a pressure lower than 1 mm Hg the helium dewar and the cavity were only partially evacuated and then flushed with clean helium gas before liquid helium was transferred.

The magnet which is left in place all the time is centered in advance, and the adjustment of the optical system is checked from time to time, in particular the sharpness of the extinction of light between crossed nicols.

Then the dewar sealed by the rubber sleeve to the cap and held by steel spring suspensions is frozen in position by filling the cap with liquid nitrogen. The precooling of the inner dewar down to 77°K is done from the outer dewar and the cap. The technique of transferring helium and the attainment of temperatures below the \( \lambda \)-point is the same as in the experiment already described.

The klystron is then switched on and its power output and frequency adjusted. The magnetic field is turned on and the angle of rotation is measured as a function of the magnetic field. During the experiment the frequency and power output of the klystron is checked as to its constancy, and the desired temperature of the liquid helium bath is adjusted by controlling the pumping speed.
3.9) Features of the Spectrometer

This spectrometer has been designed for the use of various different experiments in paramagnetic resonances. It can be used for experiments at any temperature between room temperature and 1.35°K. It allows the study of magneto-optical effects in connection with paramagnetic resonances, and having a high Q cavity and a high power klystron, it allows the study of saturation effects of paramagnetic resonances such as the influence of paramagnetic resonance saturation on the Faraday effect and the Overhauser effect. It has a high sensitivity and can detect $10^{15}$ spins of $S = \frac{1}{2}$ above noise level at room temperature as checked by means of the 41 hyperfine structure lines of a standard Mn$^{++}$ salt sample. The stability of the microwave frequency and microwave power was found to be sufficient for the long runs in low temperature experiments. The stability of the magnetic field was better than needed. The display arrangement allows observation of very broad resonance lines (up to $40 \cdot 10^3$ A/m or 500 Oe).

3.10) References

1) Elmore, W.C., Sands, M., Electronics, Experimental Techniques, McGraw Hill 1944

2) Thomas, H.A., Driscoll, R.L., Hipple, J.A.,

   Phys. Rev. 78 (1950), 787

3) Shoenberg, D., Mimeographed tables, Cambridge University, England

4) Rose-Innes, A.C., Journ. Scient. Instr. 33 (1956), 31
IV) PARAMAGNETIC RESONANCE OF CR$^{3+}$ IN GUANIDINE ALUMINIUM SULPHATE HEXAHYDRATE

4.1) Introduction

Guanidine aluminium sulphate hexahydrate (CN$_3$H$_6$)Al(SO$_4$)$_2$·6H$_2$O has been recently discovered to be ferroelectric $^1$. It is one of an isomorphous series, in which the Al can be replaced by Ti$^{4+}$, V$^{5+}$, Cr$^{3+}$, Fe$^{3+}$, all members of the series being ferroelectric. These salts grow in hexagonal plates and belong to the space group C$_3^2$ or P3lm. When this work was started the determination of the structure of this salt was not completed, but it was known that there are three Al$^{3+}$-ions in the unit cell. It was worthwhile to complete the crystallographic information with respect to the crystalline electric field of the immediate neighbours of the Al$^{3+}$ ions. For this purpose Cr was introduced as impurity into the lattice replacing Al. The ferro-electric direction is parallel to the trigonal axis. No other ferroelectric salt is known in this space group.

Ferroelectricity causes spontaneous distortion of the crystal lattice, and this may influence the paramagnetic resonance spectrum of a paramagnetic ion in such a salt, through changes in the crystalline electric field.

At the time when this work was started, the only known paramagnetic resonance spectrum of a paramagnetic ion in a known ferroelectric salt was Fe$^{3+}$ as an impurity in BaTiO$_3$ $^2$. 
Bleaney and others had noticed changes in the paramagnetic resonance spectrum of certain alums, \( \text{Cr}[\text{NH}_2\text{CH}_3](\text{SO}_4)_2\cdot12\text{H}_2\text{O} \), \( \text{Cr}(\text{NH}_4)(\text{SO}_4)_2\cdot12\text{H}_2\text{O} \) when these salts were cooled or warmed through a temperature characteristic of the salt (157°K for the \( \text{Cr(NH}_2\text{CH}_3) \)-alum, 80°K for the \( \text{Cr(NH}_4 \)-alum). It has since been shown that these salts are ferroelectric, and the temperature at which an abrupt change occurs in the paramagnetic resonance spectrum is the ferroelectric Curie temperature.

Unfortunately, guanidine aluminium sulphate hexahydrate starts to lose water of crystallization above 100°C, a much lower temperature than the estimated Curie temperature. The Curie temperature has been estimated to be above 200°C from the extrapolation of the curve of spontaneous polarisation versus temperature to zero polarisation.

4.2) The Spectrum of \( \text{Cr}^{+++} \) in \( (\text{CN}_3\text{H}_6)\text{Al(SO}_4)_2\cdot6\text{H}_2\text{O} \)

Paramagnetic resonances of \( \text{Cr}^{+++} \)-ions are well understood. \( \text{Cr}^{+++} \) has the ground state \( ^4F_{3/2} \) with \( S = \frac{3}{2} \).

The spectrum of \( \text{Cr}^{+++} \) replacing \( \text{Al}^{+++} \) in \( (\text{CN}_3\text{H}_6)\text{Al(SO}_4)_2\cdot6\text{H}_2\text{O} \) was investigated. The measurements were made on a crystal in which about 2 atom per cent of the \( \text{Al}^{+++} \) was replaced by \( \text{Cr}^{+++} \), at 3.24 cm wave-length at the following temperatures:

\( 295^\circ\text{K}, 195^\circ\text{K}, 77^\circ\text{K}, 35^\circ\text{K}, \) and at \( 4.2^\circ\text{K} \).

The temperatures were obtained as follows. \( 295^\circ\text{K} \) was the average room temperature. Deviations did not exceed
FIGURE 12

SPECTRUM OF Cr$^{+++}$ IN \([\text{C(NH}_2\text{)}_3\text{Al(SO}_4\text{)}_2 \cdot 6\text{H}_2\text{O}]

MAGNET CURRENT FOR RESONANCE vs ORIENTATION

\begin{align*}
\text{ANGLE } \theta (^\circ) & \quad \text{z } \perp \text{H} \\
-150 & \quad -120 & \quad -90 & \quad -60 & \quad -30 & \quad 0 & \quad 30 & \quad 60 \\
\text{z } \parallel \text{H} & \quad \text{z } \parallel \text{H}
\end{align*}

ROTATION ABOUT AN AXIS PERPENDICULAR TO THE TRIGONAL AXIS z
FIGURE 13
SPECTRUM OF Cr$^{+++}$
IN $[\text{C(NH}_2\text{)}_3\text{Al(SO}_4\text{)}\cdot6\text{H}_2\text{O}]$

ROTATION ABOUT THE TRIGONAL AXIS $z$

Facing page 57
### Table 1

**Measured Relative Intensities of the Lines**

|        | H || z | H ⊥ z |
|--------|------|-------|
| **Set 1** | **Set 2** | **Set 1** | **Set 2** |
| H₁ (1) → 12 | H₁ (2) → 6 | H₁ (1) → 25 | H₁ (2) → 13 |
| (H₂ (1) + H₂ (2)) → 30 | | H₂ (1) → 40 | H₂ (2) → 20 |
| H₃ (1) → 12 | H₃ (2) → 6 | H₃ (1) → 12 | H₃ (2) → 6 |

Facing page 57
1°K. 195°K is the temperature of a mixture of dry ice (CO₂) and acetone. 77.3°K is the boiling point of liquid nitrogen. The dewar was protected against diffusion of oxygen into the liquid to keep the temperature constant. The temperature 35°K was produced by desorbing helium from activated charcoal and could be maintained within about ± 3°K. 4.2°K is the temperature of boiling liquid helium.

The spectra were observed with the external magnetic field in the plane perpendicular to the trigonal axis of the crystal, and in a plane containing this trigonal axis (see Fig. 12 and 13). Two sets of axially symmetric spectra, a total of six lines, were observed, set 1 being about twice as intense as set 2, as indicated in table 1. These intensities can be explained by the assumption that there are two kinds of Cr³⁺⁺⁺ ions, one set being twice as numerous as the other. Since there are three Cr³⁺⁺⁺ ions per unit cell, two of them are magnetically equivalent.

At the dilution mentioned above, the half-power line width of all lines was about 3.2·10⁻³ A/m (≈ 40 Oe) wide at room temperature. At lower temperature the line width did not change noticeably. The line shape was approximately gaussian-lorentzian.

The signal to noise ratios observed on the oscilloscope display were about 80:1 for the strongest line and 30:1 for the smaller ones. No variation of the position of the lines was observed as the external magnetic field was rotated in the plane perpendicular to the trigonal axis. Measurements of the spectra
Table 2

$D_1$ and $D_2$ as Function of $T$

<table>
<thead>
<tr>
<th></th>
<th>$D_1$ (in cm$^{-1}$)</th>
<th>$D_2$ (in cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295°K</td>
<td>0.0576 ± 0.0005</td>
<td>0.0730 ± 0.0005</td>
</tr>
<tr>
<td>195°K</td>
<td>0.0696 ± 0.0006</td>
<td>0.0882 ± 0.0010</td>
</tr>
<tr>
<td>77°K</td>
<td>0.0822 ± 0.0010</td>
<td>0.105 ± 0.003</td>
</tr>
<tr>
<td>35°K</td>
<td>0.085 ± 0.003</td>
<td>0.109 ± 0.005</td>
</tr>
</tbody>
</table>

Extrapolated point of intersection at about $D = 0$ cm$^{-1}$ and $T = 775°K$.

$g = 1.975 ± 0.005$ for all four temperatures.
Figure 14

Graph showing the relationship between $D$ in cm$^{-1}$ and temperature $T$ in °K. Two curves are plotted:

- $D_1$
- $D_2$

The $D_2$ curve is above the $D_1$ curve, indicating that $D_2$ is generally higher than $D_1$ for the same temperature.

Temperature scale ranges from 0 to 300 °K, while the $D$ scale ranges from 0.050 to 0.110 cm$^{-1}$.
with the field rotated in the plane containing the trigonal axis show that both sets of spectra can be fitted to the spin-Hamiltonian

$$\mathcal{H} = g \beta \mathbf{H} \cdot \mathbf{S} + D \left\{ S_z^2 - \frac{1}{3} S(S + 1) \right\}$$

(1)

where $S = \frac{3}{2}$ and the $z$-axis is the trigonal axis of the crystal. $g$ is isotropic. The deviations between experimental and calculated positions of the lines are smaller than 1% for the temperatures mentioned except at $4.2^\circ K$, where the spectrum could not be described by this spin-Hamiltonian. The values of the constants $g$ and $D$ for both spectra at different temperatures are given in Table 2. The variation of the $D$'s with temperature is shown in Fig. 14. Fig. 12 shows a plot of the spectrum as a function of angle for a rotation about an axis perpendicular to the trigonal axis.

It has been shown that the Cr$^{+++}$ ions are inside a field of trigonal symmetry, they lie on the three-fold axis. Since there are three ions per unit cell, two of them are magnetically equivalent. As far as the structure of the lattice is concerned the same is true for the Al$^{+++}$ ions.

The spin-Hamiltonian (1) is diagonal in a representation with $S_z$ diagonal if the external field $\mathbf{H}$ is along the $z$-axis, the trigonal axis of the crystal. Thus the eigenvalues are easily found in this case. The positions of the lines are given by

$$\hbar \nu = g \beta H_1 + 2D$$
$$\hbar \nu = g \beta H_2$$
$$\hbar \nu = g \beta H_3 - 2D$$

(2)
To measure \( g \) with reasonable accuracy, a sample of D.P.P.H. which gives a single narrow line, 300 A/m (\( \approx 3.7 \) Oe) wide at \( g = 2.0038 \), was placed in the cavity close to the salt. It was possible to see the D.P.P.H. signal close to the central \( \text{Cr}^{+++} \) line on the oscilloscope. A measurement of the change in field necessary to displace the D.P.P.H. line from the centre of the display and place the \( \text{Cr}^{+++} \) line there, gives directly the difference between the \( g \) for D.P.P.H. and the \( g \) for \( \text{Cr}^{+++} \).

These fields were also measured by proton resonance as described in chapter III. The deviations in the magnetic field between the positions of the crystal and the proton sample were checked with the D.P.P.H. signal. The deviation was at most \( 1.6 \times 10^{-3} \) A/m (\( \approx 20 \) Oe) at \( H = 263.10^{-3} \) A/m (\( \approx 3306 \) Oe) when the distance between the proton resonance probe and the paramagnetic resonance sample was enlarged by the wall of the dewar. By extrapolation of this deviation to higher and lower fields the error in field measurements could be made smaller than 0.3%.

Knowing \( g \), the value of \( D \) can be obtained from the fields needed for the outer lines; for

\[
4D = g\beta (H_z - H_x)
\]

Another value of \( D \) can be obtained when the external field is perpendicular to the trigonal axis. In this case the Hamiltonian is

\[
\begin{pmatrix}
\frac{3}{2} g\beta H - \frac{1}{2} D & 0 & \sqrt{\frac{3}{2}} D & 0 \\
0 & \frac{1}{2} g\beta H + \frac{1}{2} D & 0 & \frac{\sqrt{3}}{2} D \\
\frac{\sqrt{3}}{2} D & 0 & -\frac{1}{2} g\beta H + \frac{1}{2} D & 0 \\
0 & \frac{\sqrt{3}}{2} D & 0 & -\frac{3}{2} g\beta H - \frac{1}{2} D
\end{pmatrix}
\]
The secular determinant factorises into two quadratic equations, and the eigenvalues are easily found. To the first order the positions of the outer lines are given by

$$\hbar \nu = g \beta H_1 - D = g \beta H_2 + D$$

hence

$$g \beta (H_1 - H_2) = 2D$$

The values of $D$ obtained from this orientation are in good agreement (difference $\leq 1\%$) with those obtained from $H$ parallel to $z$.

At intermediate angles the problem is more difficult. Since $D$ is not very small compared with $g \beta H$, it was considered that the usual way of finding the eigenvalues, namely perturbation theory, might not be as accurate as desirable. The exact Hamiltonian was diagonalized using a digital computer for a series of angles, and the line positions predicted from the spin-Hamiltonian (1) agreed with the measured values within the experimental error.

A small change in the $g$-values could be expected with a change of lattice dimensions. A slight indication of this was found but was not significant in view of the accuracy of the measurements. Two different $g$-values could be expected for the two sets of spectra. Within the experimental error, both spectra had the same value of $g$.

Several weak lines have been observed near the strongest lines, with intensities up to a tenth of the main
lines. Some of them were almost lost in noise, and it was not possible to measure their positions accurately. These lines were not classified. It is doubtful if the 9.5% abundant isotope \( \text{Cr}^{53} \) could be responsible for these lines. They are probably due to interactions of adjacent pairs of \( \text{Cr}^{+++} \) ions.

It would be interesting to investigate these lines with an apparatus of higher sensitivity.

Holden et al. \(^1\) observed that different parts of a guanidine aluminium sulphate crystal have different electrical properties. The sections of easy and hard polarisibility are shown in the Fig. 15 giving the cross section of an hexagonal plate.

\[ \text{Figure 15} \]

Therefore, great care was used to grow large crystals of good shape from which sections could be easily cut. The crystals were grown from an aqueous solution of an equimolecular mixture of guanidine sulphate and aluminium sulphate. Seeds were used, and the saturated solution was kept under one atmosphere pressure in a cupboard for about a week. The paramagnetic resonance spectrum of \( \text{Cr}^{+++} \) in crystal fragments cleaved from different parts of a large crystal plate has been examined. No difference has been observed in the spectrum. The crystals were also polarised in a strong electric field \((6 \cdot 10^5 \text{ V/m})\) in the direction of the trigonal axis, using a Whimshurst influence
machine, and depolarised in a weakening alternating electric field of 60 c/s, using a high voltage transformer and variac. These processes had no influence on the paramagnetic resonance spectrum. These values were sufficient since the coercive field is \((1 \times 10^5 - 3 \times 10^5)\) V/m and the electric dipole relaxation time is \(< 1 \times 10^{-2}\) s as measured by Holden et al. \(^1\).

It can be concluded that any changes in the values of the \(D\) caused by lattice distortions due to the ferroelectric state, are less than 1%. Investigations of Holden et al. show that the guanidine ion is responsible for the ferroelectric behaviour of this salt. From a recent detailed X-ray analysis \(^5\) it is concluded that the guanidine ion is about half the c-axis away from the Cr\(^{+++}\) ion in the [001] direction and that the immediate neighbours are the 6H\(_2\)O molecules forming a stretched octahedron. That the polarisation of the guanidine ion has no noticeable effect on the constants \(D\) also means that the octahedron is not easily deformed.

The paramagnetic properties of the Cr\(^{+++}\) ion are not very sensitive to changes of the crystalline field. The Ti\(^{+++}\) ion with a ground state \((3d)^4 \frac{2D_3}{2}\), is very sensitive to crystalline field changes. This is because the orbital wave function is a triplet in the cubic component of the crystalline field, and the wave function of the actual splittings depends strongly on the details of the components of the crystalline field of lower symmetry. I therefore tried to grow crystals with Ti\(^{+++}\) as impurity, but I have so far had no success in these efforts.
4.3) Calculations of Eigenvalues and Position of Lines for Intermediate Angles

For intermediate angles the spin-Hamiltonian is

\[ \mathcal{H} = \frac{g}{\beta} H \left( S_z \cos \Theta + S_x \sin \Theta \right) + D \left( S_z^2 - \frac{S_z^2}{4} \right) \]  

or

\[
\begin{pmatrix}
\frac{3}{2} gBH \cos \Theta + D & \frac{\sqrt{3}}{2} gBH \sin \Theta & 0 & 0 \\
\frac{\sqrt{3}}{2} gBH \sin \Theta & \frac{1}{2} gBH \cos \Theta - D & gBH \sin \Theta & 0 \\
0 & gBH \sin \Theta & \frac{1}{2} gBH \cos \Theta - D & \frac{\sqrt{3}}{2} gBH \sin \Theta \\
0 & 0 & \frac{\sqrt{3}}{2} gBH \sin \Theta & \frac{3}{2} gBH \cos \Theta + D
\end{pmatrix}
\]

Where \( \Theta \) is the angle between the external magnetic field and the trigonal axis (z) of the crystal. Division by \( D \) and substitution of \( X = \frac{g\beta H}{D} \) gives

\[
\begin{pmatrix}
\frac{3}{2} X \cos \Theta + 1 & \frac{\sqrt{3}}{2} X \sin \Theta & 0 & 0 \\
\frac{\sqrt{3}}{2} X \sin \Theta & \frac{1}{2} X \cos \Theta - 1 & X \sin \Theta & 0 \\
0 & X \sin \Theta & \frac{1}{2} X \cos \Theta - 1 & \frac{\sqrt{3}}{2} X \sin \Theta \\
0 & 0 & \frac{\sqrt{3}}{2} X \sin \Theta & \frac{3}{2} X \cos \Theta + 1
\end{pmatrix}
\]

In order to check whether the assumed spin-Hamiltonian describes the spectrum we decided to calculate the positions of the lines for the following values of \( \Theta \), the angle between the magnetic field and the crystalline axis \( \downarrow \).
\( \Theta = 0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ, 90^\circ. \)

For \( \chi = \frac{g_\beta H}{D} \) the following values are taken

2.00, 2.25, 2.50, 2.75, 3.00, .............. 7.00, 7.25.

With these values the matrix (7) has been diagonalized using the digital computer "Alwac III E" of this university.

The eigenvalues of these 154 matrices are given in the appendix to this chapter.

The transitions at a certain angle \( \Theta \) are obtained from the table of eigenvalues by finding a value \( \chi^1 \) for which the difference between consecutive eigenvalues is \( \frac{\Delta \lambda}{\Delta \chi^1} \). Interpolation between the tabulated values of \( \chi \) is necessary. Then the value of \( H \) at which the line occurs is given by

\[
H = \chi^1 \cdot \frac{D}{g_\beta} \tag{8}
\]

If \( \nu \) the wave number and \( D \) are both given in cm\(^{-1} \), then the formula

\[
H = \chi^1 \cdot \frac{D \nu}{g_\beta} \tag{9}
\]

has to be used. In the following table the fields at which transitions occur are listed in kOe.
Table III  Spectrum at $T = 295^\circ K$

average $\tilde{\nu} = 0.30867$ cm$^{-1}$

average $g = 1.975 \pm 0.005$

$\Theta = 0^\circ$

<table>
<thead>
<tr>
<th>Transition</th>
<th>Line</th>
<th>Field in kOe</th>
<th>Separation between lines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>calculated</td>
<td>measured</td>
</tr>
<tr>
<td>$3/2 \leftrightarrow 1/2$</td>
<td>$H_1$</td>
<td>2.092</td>
<td>2.093</td>
</tr>
<tr>
<td>$1/2 \leftrightarrow -1/2$</td>
<td>$H_2$</td>
<td>3.348</td>
<td>3.356</td>
</tr>
<tr>
<td>$-1/2 \leftrightarrow -3/2$</td>
<td>$H_3$</td>
<td>4.604</td>
<td>4.603</td>
</tr>
</tbody>
</table>

Set 1

$\Theta = 15^\circ$

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<th>Separation between lines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td>measured</td>
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<tr>
<td>$3/2 \leftrightarrow 1/2$</td>
<td>$H_1$</td>
<td>2.1740</td>
<td>2.170</td>
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<td>$1/2 \leftrightarrow -1/2$</td>
<td>$H_2$</td>
<td>3.3962</td>
<td>3.385</td>
</tr>
<tr>
<td>$-1/2 \leftrightarrow -3/2$</td>
<td>$H_3$</td>
<td>4.4330</td>
<td>4.425</td>
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Set 2

$\Theta = 0^\circ$

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<th>Field in kOe</th>
<th>Separation between lines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>calculated</td>
<td>measured</td>
</tr>
<tr>
<td>$3/2 \leftrightarrow 1/2$</td>
<td>$H_1$</td>
<td>1.8425</td>
<td>1.850</td>
</tr>
<tr>
<td>$1/2 \leftrightarrow -1/2$</td>
<td>$H_2$</td>
<td>3.4480</td>
<td>3.430</td>
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<tr>
<td>$-1/2 \leftrightarrow -3/2$</td>
<td>$H_3$</td>
<td>4.5958</td>
<td>4.700</td>
</tr>
</tbody>
</table>
\( \theta = 30^\circ \)

<table>
<thead>
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<th>Separation between lines</th>
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<tbody>
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| \( \theta = 45^\circ \)

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\[ \Theta = 60^\circ \]

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\[ \Theta = 75^\circ \]

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\[ \Theta = 90^\circ \]

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<td>[H_2]</td>
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<td>[H_3]</td>
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<td>0.625</td>
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</table>
4.4) The Spectrum at Low Temperatures

At lower temperatures the curves of the spectrum are geometrically similar to those at room temperature. Down to $35^\circ K$ the spectrum still has axial symmetry, since the position of the lines does not vary when the field is rotated in the plane perpendicular to the trigonal axis. Therefore, in order to test whether the spin-Hamiltonian (1) describes the spectrum at low temperatures, it is sufficient to take measurements of the positions of the lines at $H$ parallel and perpendicular to the $z$-axis. At the temperatures $T = 195^\circ K, 77.3^\circ K$ the magnetic field was measured by means of proton resonance, and at $35^\circ K$ and $4.2^\circ K$ the calibration curve of the magnet was used for the determination of the field. At all temperatures except at $T = 4.2^\circ K$, the $D$-values obtained from measurements at $H$ parallel to the $z$-axis agree with those obtained from measurements at perpendicular to the $z$-axis and the $g$-value is isotropic within the limits of the experimental accuracy. When the field is parallel to the $z$-axis the position of the centre line is given by

$$H_z = \frac{H_1 + H_2}{2}$$

which is consistent with the axial symmetry.
Table IV  Spectrum at $T = 195^\circ K$

average $\tilde{\nu} = 0.30930$ cm$^{-1}$
average $g = 1.980 \pm 0.005$

$\Theta = 0^\circ$

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<tr>
<td></td>
<td>calculated</td>
<td>measured</td>
</tr>
</tbody>
</table>

**Set 1**

| $3/2 \leftrightarrow 1/2$  | $H_1$ | 1.8470 | 1.828 | 1.5078 | 1.537 |
| $1/2 \leftrightarrow -1/2$ | $H_2$ | 3.3548 | 3.365 | 1.5072 | 1.496 |
| $-1/2 \leftrightarrow -3/2$| $H_3$ | 4.8620 | 4.861 |         |       |

**Set 2**

| $3/2 \leftrightarrow 1/2$  | $H_1$ | 1.4418 | 1.394 | 1.9130 | 1.971 |
| $1/2 \leftrightarrow -1/2$ | $H_2$ | 3.3548 | 3.365 | 1.9130 | 1.921 |
| $-1/2 \leftrightarrow -3/2$| $H_3$ | 5.2678 | 5.286 |         |       |

$\Theta = 90^\circ$

<table>
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<tr>
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<td>measured</td>
</tr>
</tbody>
</table>

**Set 1**

| $3/2 \leftrightarrow 1/2$  | $H_1$ | 4.0991 | 4.106 | 0.8766 | 0.894 |
| $1/2 \leftrightarrow -1/2$ | $H_2$ | 3.2225 | 3.212 | 0.5986 | 0.607 |
| $-1/2 \leftrightarrow -3/2$| $H_3$ | 2.6239 | 2.605 |         |       |

**Set 2**

| $3/2 \leftrightarrow 1/2$  | $H_1$ | 4.2252 | 4.316 | 1.0900 | 1.204 |
| $1/2 \leftrightarrow -1/2$ | $H_2$ | 3.1352 | 3.112 | 0.6846 | 0.682 |
| $-1/2 \leftrightarrow -3/2$| $H_3$ | 2.4506 | 2.430 |         |       |
Table V. Spectrum at $T = 77.3^\circ K$

average $\bar{\nu} = 0.30990$ cm\(^{-1}\)

average $g = 1.975 \pm 0.005$

$\Theta > 0^\circ$

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Set 1

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<td>5.6730</td>
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$\Theta = 90^\circ$

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### Table VI Spectrum at $T = 35^\circ K$

average $\tilde{\nu} = 0.3098$ cm$^{-1}$

average $\varrho = 1.975 \pm 0.005$

$\varphi = 0^\circ$

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$\varphi = 90^\circ$

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4.5) The Eigenvalues of the Energy Matrix

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1) Holden, A.W., Matthias, B.T., Merz, W.J., Remeika, J.P.,
   Phys. Rev. 98 (1955), 546
   Phys. Rev. 101 (1956), 962

2) Horning, A.W., Jaynes, E.T., Weaver, H.E.,
   Phys. Rev. 96 (1954), 1703

   Phil. Mag. 42 (1951), 441
   Bowers, K.D., Owen, J., Reports Progr. Phys. 18 (1955), 338

4) Bowers, K.D., Owen, J., Reports Progr. Phys. 18 (1955), 304

5) Geller, S., private communication, Bell Telephone Laboratories
V) PARAMAGNETIC RESONANCE OF Fe$^{+++}$ IN AMMONIUM PENTACHLOROINDATE HYDRATE

5.1) Introduction

The interest in ammonium pentachloroindate hydrate, \((\text{NH}_4)_2[\text{InCl}_5\cdot\text{H}_2\text{O}]\), is due to the fact that In-nuclei have a large nuclear electric quadrupole moment, a large nuclear magnetic moment, and that there are many known \(\gamma\)-active In-isotopes, which altogether makes this salt suitable for Pound's method of nuclear alignment. Here the nuclear spin system is cooled down to the temperature of the lattice using the interaction of the nuclear electric quadrupole moment with the field gradient of the lattice. For the magnetic cooling of the lattice to very low temperatures one simply replaces a certain percentage of the In$^{+++}$ ions by trivalent paramagnetic ions of the iron group. In order to calculate the ultimately attainable low temperature the zero magnetic field splitting of the ground state of the paramagnetic ions in the lattice has to be known. This initial splitting can be found by paramagnetic resonances. Usually two investigations at two different microwave frequencies of resonance have to be made. The experimental data then give two sets of energy values depending on the frequency of investigation from which the initial splitting can be extrapolated.

These two investigations can be done in this low temperature physics laboratory since both an X-band and a K-band
Figure 16

\[
\begin{align*}
  c & = (120) \\
  q & = (010) \\
  n & = (120) \\
  r & = (101) \\
  a & = (100) \\
  q & = (011)
\end{align*}
\]
5.2) Some Crystallographical Details

\[(\text{NH}_4)_2\left[\text{InCl}_5\cdot\text{H}_2\text{O}\right]\] grows in orthorhombic double pyramids which belong to the symmetry class \(D_{2h}^{16}\). The ratio of the axes is

\[a : b : c = 0.9668 : 1 : 1.4005\]

The In\(^{+++}\) ions sit in the centre of a distorted octahedron of five Cl\(^-\) ions and one H\(_2\)O dipole, and there are four molecules in the unit cell.

This salt is isomorphous with \((\text{NH}_4)_2\left[\text{FeCl}_5\cdot\text{H}_2\text{O}\right]^2\), and its axes ratio is

\[a : b : c = 0.719 : 1 : 1.398\]

(where \(a = 7.09\ \text{Å}, b = 9.85\ \text{Å}, c = 13.78\ \text{Å}\)). Fe\(^{+++}\) ions go easily into the lattice of the In-salt forming mixed crystals of any desired concentration.

5.3) The Experimental Details

Crystals of about optimum size were grown, in which 10% of the In\(^{+++}\) ions were replaced by Fe\(^{+++}\) ions. Test experiments with these crystals show that no signal strength would be obtained above 77\(^\circ\)K. The signal strength increases to a maximum at about 25\(^\circ\)K. Below 25\(^\circ\)K the resonance saturates easily. The application of a lower power level to the crystal did not result in good signal strengths. Therefore, the salt
was investigated at about \(25^\circ\text{K}\).

To attain this temperature a charcoal container was attached to the cavity with wood's metal and the wanted temperature maintained by desorbing helium vapour by pumping from the charcoal which was immersed in liquid helium before the experiment started. The temperature was indicated by a gas thermometer. Each time when the helium was used up the experiments were stopped and a new liquid helium transfer was made. Only so much liquid helium was transferred as was necessary to soak the charcoal.

The crystal was attached to the choke plunger of the cavity by means of teflon supports which were shaped into a wedge or groove having the correct angle for two crystal faces to fit into it. Then the crystal was fixed in position with silk threads and cement.

In this way the crystal axis was aligned with respect to the magnetic field and to the axis of rotation. The wedges could be made on the milling machine to an accuracy of about \(\pm \frac{1^\circ}{2}\). The alignment of the crystal axis to the axis about which the crystal had to be rotated, however, could not be made better than to an accuracy of \(\pm 2^\circ\).

5.4) The Spectrum of \(\text{Fe}^{+++}\) in \((\text{NH}_4)_2\text{InCl}_5\cdot\text{H}_2\text{O}\)

The effective spin of a \(\text{Fe}^{+++}\) ion in an orthorhombic lattice can be either \(S' = \frac{1}{2}\) or \(S' = \frac{5}{2}\).

The observed lines at \(25^\circ\text{K}\) had a line width of about
Prominent lines in the 3 cm. paramagnetic resonance spectrum of iron in \((\text{NH}_4)_2[\ln \text{Cl}_5 \cdot \text{H}_2\text{O}]\). Magnetic field perpendicular to the crystal axes. Magnet current for resonance vs orientation.

Rotation about \(a\)-axis.
Rotation about b-axis
Rotation about c-axis
40 Oe (3200 A/m). The signal to noise ratio was about 10:1 and the line shape was neither gaussian nor lorentzian.

The spectra were observed with the external magnetic field in the plane perpendicular to the a-axis, then to the b-axis, then to the c-axis, and the magnetic field of lines measured as function of the rotation angle of the crystal with respect to the magnetic field direction as shown in the figures.

Because of the symmetry of the crystal only two spectra are seen with the external field perpendicular to the crystal axes. Slight misalignment of the crystal axis causes the lines to be split. If it is assumed that the spin-Hamiltonian of each ion has axial symmetry, it is possible to obtain the directional cosines of the axis of each ion from these measurements. The lines should all display maxima or minima in field, when the external field makes a maximum or minimum angle with the ionic axis. This happens when it is either perpendicular to an ionic axis or when it lies along the projection of that ionic axis on one of the crystal planes. Referring to Fig. 16, in either case

\[ \tan \alpha \cdot \tan \beta \cdot \tan \gamma = 1 \quad (1) \]

\[ \sum_{i=1}^{3} \ell_i^2 = 1 \]

It is not certain that the spin-Hamiltonian has axial symmetry, for two different sets of angles \( \beta \) are observed which satisfy equation (1) within the limits of experimental error.

From each of these we derive the following possibilities for the directional cosines:
Set I
\[ \varphi_a = 77^0, \quad \varphi_b = 11^0, \quad \varphi_c = 50^0 \]
gives \[ \ell_i = \pm 0.1860, \quad \ell_x = \pm 0.2212, \quad \ell_z = \pm 0.9578 \]
or \[ \varphi_a = 13^0, \quad \varphi_b = 79^0, \quad \varphi_c = 40^0 \]
gives \[ \ell_i = \pm 0.7576, \quad \ell_x = \pm 0.6357, \quad \ell_z = \pm 0.1488 \]

Set II
\[ \varphi_a = 17^0, \quad \varphi_b = 70^0, \quad \varphi_c = 50^0 \]
gives \[ \ell_i = \pm 0.6636, \quad \ell_x = \pm 0.7123, \quad \ell_z = \pm 0.22805 \]
or \[ \varphi_a = 73^0, \quad \varphi_b = 20^0, \quad \varphi_c = 40^0 \]
gives \[ \ell_i = \pm 0.3289, \quad \ell_x = \pm 0.2762, \quad \ell_z = \pm 0.9033 \]

The directional cosines of the various ionic axes are obtained by permutating the signs in the table above. To determine which of these sets is appropriate requires detailed calculation of the spin-Hamiltonian.

The spin-Hamiltonian for the rotational spectrum about a principle axis has to be calculated and the described spectrum to be checked experimentally. Here the difficulty arises of the proper alignment of the crystal, as the attainable accuracy of the alignment of the principle axis along the axis of rotation is limited due to the smallness of the crystal.

The three spectra obtained by rotations about the three crystal axes separately, theoretically give enough information
to derive the spin-Hamiltonian. It was considered that the completion of these investigations would be rather laborious both experimentally and theoretically. The investigations had to be stopped with the results obtained so far for the benefit of the study of the influence of paramagnetic resonance on the paramagnetic Faraday effect.

5.5) Suggestions for Continuation of These Experiments

The difficulty in this problem is the correct mounting of the crystal. A larger crystal makes mounting easier and hence better accuracy of the orientation of the crystal axis with respect to the magnetic field is obtained. Then, unfortunately, the size of the crystal would be by far greater then the optimum size, and the signal strengths would decrease.

Another possibility is to design a larger cavity in which half the size of the crystal is equal to the optimum size of a $\text{TE}_{101}$ cavity. This would be a cavity operating in the $\text{TE}_{201}$ mode.

5.6) References

1) Wallace, R.C., Zeitschr. Krist. 49 (1911), 417
VI) INFLUENCE OF PARAMAGNETIC RESONANCE SATURATION ON THE PARAMAGNETIC FARADAY EFFECT

6.1) Introduction

The Faraday effect in paramagnetic salts (i.e. the rotation of the plane of polarisation of light propagated through the salt in the direction of an applied external magnetic field) is usually very much larger than the effect in other substances. For instance, in neodymium ethylsulphate at 1°K, the effect is about 2000 times as large as in the isomorphous but diamagnetic lanthanum ethylsulphate. This extra effect we will call the "paramagnetic Faraday effect". In neodymium ethylsulphate, the paramagnetic Faraday effect is caused by interaction of the electric vector of the light wave with the unpaired 4f electrons in the neodymium ion, the same electrons as those which are responsible for the paramagnetism of the salt. It can be shown that, to a first approximation, the paramagnetic rotation of the plane of polarisation of light is proportional to the magnetic moment of the salt. If the salt is exposed to microwave radiation of the correct frequency to cause resonance in the paramagnetic ion, and if the microwave power is large enough to cause noticeable saturation of this resonance, the populations for the various energy levels of the paramagnetic ion are changed from the equilibrium values given by Boltzmann's theorem, and the magnetic moment of the salt is reduced. In this case, a reduction in the angle of rotation of
the plane of polarisation of the light should be noticed. This effect was first predicted by Kastler \cite{Kastler}.
A complete theory of this effect has been worked out by Opechowski \cite{Opechowski}. We shall next present a simpler theory than that given by Opechowski; this is followed by a description of experiments in which attempts were made to observe this effect.

6.2) A Simple Theory of the Faraday Effect

According to dispersion theory, the refractive index of a dielectric medium is given by:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\varepsilon^2}{3 \eta \gamma^2 \omega^2} \sum \frac{N_i (\nu_i^2 - \nu^2)}{(\nu_i^2 - \nu^2)^2 + \nu^2 \gamma_i^2}$$

(1)

where $N_i$ is the number of electrons per cm$^3$ with a resonant frequency $\nu_i$, $\nu$ the frequency of the light, $\gamma_i$ the damping constant of the $i$th oscillating electron, $\varepsilon$ and $\gamma_e$ the charge and mass of an electron respectively.

Here the medium is considered to be a gaseous system of dipoles where interactions are neglected. For our case we can further simplify the expression by omitting the damping constants $\gamma_i$ and assuming $n \approx 1$, $n^2 + 2 \approx 3$. Thus we obtain the simplified expression

$$n - 1 = \frac{\varepsilon^2}{2 \eta \gamma^2 \omega^2} \sum \frac{N_i}{\nu_i^2 - \nu^2}$$

(1a)

Larmor's theorem states that the equations of motion of an electron in an external magnetic field $\mathcal{H}$, are the same as the equations of motion of the same electron in a zero external
magnetic field, but in a frame of reference rotating about the direction of \( \mathcal{H} \) with an angular velocity

\[ \nu_L = \frac{\mu_0 \ell}{4 \pi m_e} \mathcal{H} \text{ revolutions/sec.} \]

This angular velocity is called the "Larmor frequency". We therefore replace the external magnetic field in this problem by a rotating frame of reference. The only kind of polarised light, propagated along the axis of rotation of the reference frame, whose polarisation is independent of the rate of rotation, is circularly polarised light. Therefore, we work out the refractive indices of the medium for circularly polarised light, and treat any other kind of polarised light as a linear superposition of two circularly polarised beams. The appropriate normal modes of oscillation of the electrons are also "circular motions" in a plane perpendicular to the axis of rotation. When a transformation is made from rotating coordinates to fixed coordinates, the oscillation frequencies of the electrons are changed to \( \nu_i \pm \nu_L \), the sign depending on the sense of the "motion" about the axis of rotation. We notice that circularly polarised light can excite only the motion with the same sense as the light. Thus the electron resonance frequency is different for the two kinds of circularly polarised light, and in equation (1a) \( \nu_i \) must be replaced by \( \nu_i \pm \nu_L \).

The foregoing is essentially a classical picture of the Zeeman effect. In the quantum theory of the Zeeman effect (both the simple and the anomalous effect), a single emission
or absorption line is split into two (or more in the anomalous Zeeman effect) lines, and each line emits or absorbs along the direction of the magnetic field only circularly polarised light. We can use the classical dispersion formulae (equation 1a) in the quantum case provided we make the following correspondences:

(i) $\nu_i$ in (1a) shall be replaced by $\nu_i \pm \delta \nu$, where $\delta \nu$ is the Zeeman displacement of the absorption line for light of the appropriate polarisation.

(ii) $N_i$ in (1a) shall be the number of electrons per $m^3$ in that quantum state which permits them to absorb light of the appropriate polarisation at the frequency $\nu_i \pm \delta \nu$.

(iii) $e$ and $m_e$ shall be replaced by appropriate effective charges and masses.

As is well known, the rotation of the plane of polarisation of a beam of plane polarised light transmitted by such a system is proportional to the phase difference $\varphi$ between the two circularly polarised components of this beam, caused by the fact that these circularly polarised components travel with different velocities. It is proportional to $n_- - n_+$, where $n_-$ and $n_+$ are the refractive indices of the medium for the two circularly polarised components.

This phase difference after a path $\ell$ is given by

$$\varphi = (n_- - n_+) \frac{2 \pi \nu}{c} \ell$$

and the angle of rotation

$$\theta = (n_- - n_+) \frac{4 \pi c}{\ell} d$$

(2)
Let us now consider the simple case of one zero field absorption line which is split into two components by a magnetic field. Then

\[
n_- - n_+ = \frac{e^2}{2\hbar \omega_e} \left\{ \frac{N_+}{(\gamma_0^2 + S\gamma^2)^2} - \frac{N_-}{(\gamma_0^2 - S\gamma^2)^2} \right\}
\]

Thus

\[
N_- - N_+ = \frac{e^2}{2\hbar \omega_e} \left\{ \frac{N_+ + N_-}{2} \frac{4\gamma_0 S\gamma}{(\gamma_0^2 - \gamma^2)^2} + \frac{N_- - N_+}{N} \frac{N}{\gamma_0^2 - \gamma^2} \right\}
\]

At low temperatures and in large magnetic fields, the second term in (3) is by far the largest. It is seen to be proportional to

\[
\frac{N_- - N_+}{N_- + N_+}
\]

i.e. to the magnetic moment of the specimen, and presents the paramagnetic rotation. In thermal equilibrium \(N_-\) and \(N_+\) are given by the Boltzmann distribution formula.

When the energy levels are \(E_- = E_0 + \mu_0 H\)

\[\text{and } E_+ = E_0 - \mu_0 H\]

where \(\mu\) is the magnetic moment of the atom, the populations are accordingly

\[
N_- = \frac{N \cdot e^{-\frac{\mu_0 H}{kT}}}{e^{\frac{\mu_0 H}{kT}} + e^{-\frac{\mu_0 H}{kT}}} \text{ and } N_+ = \frac{N \cdot e^{\frac{\mu_0 H}{kT}}}{e^{\frac{\mu_0 H}{kT}} + e^{-\frac{\mu_0 H}{kT}}}
\]
then the second term becomes proportional to

\[
\tan \hbox{hyp} \frac{\mu H}{kT}
\]  

(4)

It should be noticed that a very simplified picture of the Faraday effect has been used. In particular the effects of spin-lattice broadening and saturation broadening have been neglected.

6.3) Influence of Paramagnetic Resonance on the Paramagnetic Rotation

The application of a strong microwave field of the resonant frequency tends to equalize the population of the Zeeman levels, and hence reduces the angle of rotation of the plane of polarisation of the transmitted light.

In the accurate theory of this effect, worked out by Opechowski 2), the average electric polarisability tensor of polarised light for a medium containing paramagnetic atoms is introduced in the quantum mechanical description of the Faraday effect. The tensor is complex, consisting of a Hermitian and an anti-Hermitian part. The imaginary of the Hermitian tensor determines the Faraday rotation and the double refraction respectively; the anti-Hermitian part determines the absorption. If, besides light, microwave radiation, inducing only magnetic dipole transitions, is propagated in the medium, additional terms occur in the polarisability tensor. Opechowski calculated these additional terms and applied them to the case of the paramagnetic rotation.
When the frequency of the microwave radiation is close to the resonance frequency for an allowed magnetic dipole transition he obtains for the change in paramagnetic rotation for the simple case of two energy levels \((S' = \frac{1}{2})\) whose contributions to the rotations are \(+A\) and \(-A\)

\[
\Delta \varphi = M_{s's} \lambda A \tan \text{hyp} \frac{\omega H}{kT}
\]

\[
M_{s's} = \frac{\frac{1}{2} \left| \mu_{s's} \hat{H} \right|^2 \frac{\hbar \omega}{\epsilon_H H}}{\left| \mu_{s's} \hat{H} \right|^2 + \left| \mu_x \hat{H} \right|^2 + (\hbar \omega - \epsilon_H H)^2}
\]

where \(\mu_{s's}\) is the matrix element of the magnetic dipole moment transition between the states \(S'\) and \(S\).

\(\hat{H}\) is the amplitude of the magnetic field of the microwave radiation, \(\tau_L\) the spin-lattice relaxation time, \(\omega\) the angular frequency of the microwave field \(\hat{H}\), \(H\) the average constant magnetic field in the direction of the optic axis, the z-axis of the crystal. The z-components of the magnetic moment of the levels designated by \(S'\) and \(S\) are used in the Boltzmann factors, and since the microwave field is perpendicular to the magnetic field \(H\), the x-components of the matrix elements of the magnetic dipole transitions \(\mu_{s's} = \mu_x\) have to be used.

Thus the relative change of the paramagnetic rotation is given by

\[
\frac{\Delta \varphi}{\varphi} = 2 \cdot M_{s's}
\]

(6)

When the resonance condition is fulfilled \(\omega = \mu_{s's} H\) we
It can be easily seen that the change in rotation becomes noticeable when the ratio

$$\frac{\mu_x \hat{H} \tau_L}{\hbar} \geq 1$$

(8)

The larger the spin-lattice relaxation time and the larger the applied microwave field is the larger the quantity $\frac{\Delta \rho}{\rho}$ will be.

The spin-spin relaxation time $\tau_s$ has not been taken into account by Opechowski, although it is important in saturation calculations as we see in the following section.

6.4) Saturation Considerations

Let us consider a system of magnetic dipoles in an external magnetic field with energy levels separated by $2(\mu_x H)$ spins with $S = \frac{1}{2}$. If the temperature of this spin-system is equal to the lattice temperature ($T_s = T$) then the population of the levels will be given by the Boltzmann distribution

$$N_+ = N_- e^{\frac{2 \mu_x H}{k T_s}}$$

where $N_-$ and $N_+$ are the number of dipoles in the lower and upper level respectively. The intensity of paramagnetic resonance absorption depends on the difference in occupation of
the two levels of the spins. Let us call
\[ N_\downarrow - N_\uparrow = n \]
the excess number in the lower state. \( n \) is reduced when microwave transitions between the levels concerned occur; \( T_s \) will become larger than \( T \). From that instant when the microwave field is switched off, \( n \) increases due to the spin-lattice relaxation to its former value \( n_0 \), which is the excess number when the system is in thermal equilibrium again. The rate of change of \( n \) which is supposed to be proportional to \( n_0 - n \) and also dependent on the spin-lattice relaxation time \( T_L \), is given by
\[ \frac{dn}{dt} = \frac{n_0 - n}{T_L} \]
When microwave radiation is applied a term \( 2nP \) has to be subtracted. \( P \) is the transition probability and \( 2n \) means that each upward transition reduces \( n \) by 2.
\[ \frac{dn}{dt} = \frac{n_0 - n}{T_L} - 2n \, P \] (9)

The transition probability between states designated by the magnetic quantum numbers \( M \) and \( M' \) is given by
\[ P_{M \rightarrow M'} = \frac{1}{2} \gamma^2 \hat{H}^2 |\langle M | S | M' \rangle|^2 f(v) \]
where \( \langle M | S | M' \rangle \) is the matrix element of the electron spin operator, \( f(v) \) is the normalised line shape function, \( \gamma = \frac{g \beta}{\hbar} \) the gyromagnetic ratio, \( \hat{H} \) the amplitude of the microwave field.

Since the microwave magnetic field is applied perpendicular to the external field, the non diagonal matrix elements are zero except when \( |M - M'| = 1 \). Hence
\[ |\langle M | S | M' \rangle|^2 = \frac{1}{2} (S + M)(S - M + 1) \]

For \( S = \frac{1}{2} \) we obtain

\[ \mathcal{P}_{M \rightarrow M-1} = \frac{i}{4} \gamma^2 \hat{H}^2 f(v) \]

An approximation for \( f(v) \) according to Bloembergen is given by means of the spin-spin relaxation time \( \tau_s \). Because of the normalisation, the maximum of \( f(v) \) will be large for narrow lines and small for broad lines. Thus \( \frac{1}{f(v)_{\text{max}}} \) is a rough measure for the line width which is proportional to \( \frac{1}{\tau_s} \). Bloembergen's definition of \( \tau_s \) is \( \tau_s = 2 \tau_s = f(v)_{\text{max}} \). Thus

\[ \frac{dn}{dt} = \frac{n_s - n}{\tau_L} - n \gamma^2 \hat{H} \tau_s \]

When a steady state has been reached, \( \frac{dn}{dt} = 0 \). We call the steady state value of the excess number \( n_s \) and write

\[ \frac{n_s}{n_o} = \frac{1}{1 + \gamma^2 \hat{H}^2 \tau_s \tau_L} = \mathcal{Z} \quad (10) \]

If the microwave field is applied of which the amplitude \( \hat{H} \) is large, \( n_s \) and hence \( \frac{n_s}{n_o} \) become quite small, and the spin temperature high. The above ratio is called the saturation factor \( \mathcal{Z} \). For 50% saturation for instance we obtain

\[ \gamma^2 \hat{H}^2 \tau_s \tau_L = 1 \]

6.5) Experimental Aspects

a) Estimation of the Required Power of the Microwave Field

The required amplitude \( \hat{H} \) of the microwave field follows from the condition

\[ \gamma^2 \hat{H}^2 \tau_L \tau_s \geq 1 \]
or using Opechowski's condition which has been changed into a form that takes the spin-spin relaxation time into account

$$\left( \frac{\mu_\perp}{\mu} \right)^2 \frac{1}{2} \gamma^2 \tau_L \tau_s \geq 1$$

(11)

Both conditions are of the same order of magnitude. The latter considers the magnetic dipole transition in an alternating magnetic microwave field perpendicular to the constant field.

Now we shall calculate \( \beta \) for our case of \( \text{Nd}^{+++} \), then estimate \( \tau_L \) and \( \tau_s \) in order to work out the required amplitude for a 50\% change in the paramagnetic Faraday effect.

The ground state of the \( \text{Nd}^{+++} \) ion is \( ^4S^1 \) \( \frac{1}{2} \). The \( C_{3h} \) symmetry of the crystalline electric field splits the ground state into 5 Kramers doublets. Paramagnetic resonance transitions are allowed only within three of them. At low temperatures only one doublet is populated, and the effective spin \( S = \frac{1}{2} \). The magnetic moment perpendicular to the external field is

$$\mu_\perp = \frac{1}{2} \sqrt{2} g' \beta$$

The splitting factor parallel to the magnetic field was measured at 4.2\(^0\)K, \( g_y = 3.45 \pm 0.05 \), in good agreement with Scovil's value for the diluted salt \(^4\). We then obtain \( \beta = 2.5 \nu \beta \). \( \tau_L \) and \( \tau_s \) can only be estimated. A lower limit for the order of magnitude of \( \tau_L \) can be obtained from the specific heat investigations on \( \text{Nd}-\text{ethylsulphate} \) by L.D. Roberts et al. \(^5\) who found that the reactive component of the adiabatic susceptibility near 1\(^0\)K is independent of frequency between 300 and 1200 c/s.
The electronic contribution to the specific heat was found entirely due to dipole-dipole interaction; spin-lattice relaxation and thermal conductivity become negligible.

Therefore, it is safe to assume that \( \tau_L \) is larger than \( \frac{1}{300} \) s. Let us take \( \tau_L = 3 \cdot 10^{-3} \) s.

An approximation for \( \tau_s \) can be easily made using Bloembergen's definition

\[
\tau_s = \frac{1}{2} \left[ \frac{1}{g' \beta} \right]^{\frac{1}{2}}
\]

\( f(\nu) \) is the maximum of the normalised line shape function and is approximately \( \frac{1}{\Delta \nu} \) (Bleaney and Stevens \(^6\)), the frequency difference between half-power points of the absorption line.

Thus

\[
\tau_s = \frac{\pi}{g' \beta} \frac{1}{\Delta H} = \frac{1}{2} \frac{\hbar}{g' \beta} \frac{1}{\Delta H}
\]

The line width \( \Delta H \) was measured by Scovil \(^7\) for \( H \) parallel to the optic axis and \( T = 20^\circ\text{K} \).

Using these values we obtain for \( \tau_s \approx 2.5 \cdot 10^{-9} \) s

\[
\Delta H = 32 \cdot 10^3 \frac{A}{\mu_0} (\approx 400 \text{ Oe}) \quad \beta = 1.165 \cdot 10^{-29} \text{ V}^3 \text{ m}^{-1}
\]

\[\mu_0 = 2.5 \beta \quad \hbar = 6.62 \cdot 10^{-27} \text{ Joule} \cdot \text{s} \quad \tau_L = 3 \cdot 10^{-3} \text{ s}\]

From equation (11) \( \hat{H} \) can be computed

\[
\hat{H} = \frac{\mu}{\mu_0} (\tau_L \tau_s)^{-\frac{1}{2}}
\]

Thus we obtain

\[
\hat{H} \approx 4 \frac{A}{\mu_0} (\approx 5 \cdot 10^2 \text{ Oe})
\]

as the condition for the microwave field. We shall compare this estimate in the following calculations of the available power.
b) Estimation of the Available Power Level

The absorbed power of the paramagnetic sample is

\[ \mathcal{P}_s = \frac{\omega}{2} \mu_0 \int_K X'' H^2 dV_s \]  

(12)

The meaning of the symbols is given in chapter II. \( X'' \) is the imaginary part of the radio frequency susceptibility of a paramagnetic sample. Its magnitude parallel to the magnetic field direction is \( 6) \)

\[ X'' = \frac{\pi}{\mu_0} \frac{g_{\perp}^2 N_r}{8 \hbar T} \nu \beta(\nu) \left\{ \frac{S(S+1) - M(M-1)}{2S+1} \right\} \]  

(13)

where \( N_r \) is the number dipoles per unit volume. This formula is only valid when power saturation effects are negligible.

As we consider in our case the power saturation of the resonance, the susceptibility has to be multiplied with the saturation factor \( \mathcal{Z} \) (see equation (7) and (10)), and we obtain

\[ X''_{\text{sat}} = \frac{X''}{1 + \gamma^2 \mathcal{H}^2 \tau_L \tau_s} \]  

(14)

For a 50% saturation of the resonance and for \( S = \frac{1}{2} \),

\[ \Delta \mathcal{H} = 32 \cdot 10^3 \text{A} \omega \approx \beta(\nu) = \frac{4}{g_{\parallel} \hbar} \frac{1}{\Delta \mathcal{H}} , \quad T = 1.5 \text{ K} , \quad g_{\parallel} = 3.45 , \quad \nu = 9 \cdot 10^9 \text{s}^{-1} \]

\[ N_r = 1.6 \cdot 10^{19} \text{ Nd-atom per m}^3 \]

which number corresponds to an approximately optimum size sample of Nd(C\(_2\)H\(_5\)SO\(_4\))\(_3\) \cdot 9H\(_2\)O, the absorbed power becomes

\[ \mathcal{P}_s = 1.6 \cdot 10^{-5} \frac{\text{A}}{\text{m}} \mathcal{H}^2 \]  

(15)

Using the result from the section above, \( \mathcal{H} \approx 4 \frac{\text{A}}{\text{m}} \) we obtain
\[ P_s = 0.25 \text{ mW} \]

as the estimated power level for 50% saturation. For later use the expression for any degree of saturation is

\[ P_s = \frac{3.2 \cdot 10^{-5} \frac{W}{(\text{A/m})^2} \frac{H^2}{1 + 7.67 \cdot 10^8 \frac{A^2}{\text{cm}}}} \]

(16).

A certain amount of power \( P_L \) is dissipated in the walls of the cavity resonator, in the dielectric medium of the sample and its teflon holder. \( P_L \) is related to the peak value of the field energy stored in the cavity by means of the quality factor \( Q \)

\[ Q_L = \frac{\gamma v}{P_L} \quad (17a) \]

or when paramagnetic resonance absorption is present

\[ Q'_L = \frac{\gamma v}{P_L + P_s} \quad (17b) \]

The amount of \( P_L \), which is dissipated in the walls of the cavity, can be calculated. However, \( P_L \) as a whole can be measured calorimetric by the amount of evaporated helium per second. \( Q_L \) can be measured, and the peak value of the stored energy can be calculated.

The unloaded \( Q_{uL} \) is 6200 at room temperature and when loaded with a sample of optimum size about 4500. At 4.2°C the loaded \( Q_L \) is about 9000 when the microwave strip is critically coupled into the cavity. The error of the measurement of \( Q_L \) may be 10%. The output coupling was kept very small, just to obtain an indication whether the cavity was tuned to resonance. At resonance, with \( Q_L = 9000 \), and at a temperature of 4.2°C, \( P_L \) was found to be 140 mW ± 10%. Thus the klystron is capable of
delivering 140 mW to the cavity via the transmission line.

When no paramagnetic resonance absorption is present, $P_L$ and $Q_L$ determine $\hat{\mathcal{W}}$, which contains the amplitude $\hat{H}$ of the magnetic microwave field. Hence $\hat{H}$ can be calculated. In order to work out $\hat{\mathcal{W}}$ from the geometry of the cavity resonator of this spectrometer let us replace the cavity by an equivalent box resonator having the same volume, the same mode of oscillation and resonance frequency (as described in chapter III).

In a rectangular box resonator with dimensions $a$, $b$, $c$, $a = c$, the $TE_{101}$ mode of oscillation has the amplitudes

$$\hat{H}_x = -j \hat{H} \sin \left( \frac{\pi}{a} x \right) \cos \left( \frac{\pi}{c} z \right) e^{j \omega t},$$
$$\hat{H}_y = 0,$$
$$\hat{H}_z = j \hat{H} \cos \left( \frac{\pi}{b} y \right) \sin \left( \frac{\pi}{c} z \right) e^{j \omega t}.$$

Thus

$$\hat{\mathcal{W}} = \mu_0 \frac{\hat{H}^2}{2} \int_{x=0}^{a} \int_{y=0}^{b} \int_{z=0}^{c} \left\{ \sin^2 \left( \frac{\pi}{a} x \right) \cos^2 \left( \frac{\pi}{c} z \right) + \cos^2 \left( \frac{\pi}{b} y \right) \sin^2 \left( \frac{\pi}{c} z \right) \right\} dx dy dz$$

$$\hat{\mathcal{W}} = \mu_0 \hat{H}^2 \frac{a^2 b}{4}, \quad \frac{a^2 b}{4} = 1.275 \times 10^{-6} \text{ m}^3$$

From (17a) we obtain

$$\hat{\mathcal{W}} = \hat{\mathcal{W}} \frac{1}{2} = 2.15 \times 10^{-8} \text{ J} \mu \text{e}, \pm 10\%$$

Hence, this spectrometer generates

$$\left| \hat{H}_x \right| \approx \hat{H} \approx 118 \frac{A}{m} \pm 10\% \quad (\text{or} \ 1.5 \ \text{Oe})$$

in the absence of paramagnetic resonance at the point of the sample $x = \frac{a}{2}$, $y = \frac{b}{2}$, $z \approx 0$. 
Thus the available power supplies a microwave field whose amplitude is approximately thirty times as strong as necessary for a 50% decrease of the Faraday effect, under the assumption that \( \tau_L = 3 \cdot 10^{-3} \) s.

c) Purity Requirements of the Crystal

The requirement of purity of Nd\((C_2H_5SO_4)_3\cdot9H_2O\) is not too stringent. A small amount of other rare earth components can be tolerated. The most probable impurity is cerium. Let us consider that 1 atom per cent of Nd\(^{+++}\) has been replaced by Ce\(^{+++}\). The effect will be a slight increase of the paramagnetic Faraday rotation, as the Faraday effect of the cerium salt is larger than that of the neodymium salt.

More important for saturation experiments is the influence of the impurities on the relaxation times \( \tau_L \) and \( \tau_\perp \). Experiments have been done to study the effect of Ce\(^{+++}\) ions on the spin-lattice relaxation time of certain energy levels of Gd\(^{+++}\). For instance, Ce\(^{+++}\) has a strong effect on \( \tau_L \) when the splittings for Ce\(^{+++}\) and Gd\(^{+++}\) overlap \(^8\). In a crystal of La\((C_2H_5SO_4)_3\cdot9H_2O\) where 0.5 atom per cent of La has been replaced by Gd and 0.2 atom per cent by Ce, \( \tau_L \) is reduced by a factor 7, here the relative percentage of Ce replacing Gd is 40%.

Investigations on a concentrated Ce\((C_2H_5SO_4)_3\cdot9H_2O\) crystal \(^7\) also show a reduction of the relaxation time. The influence of only 1 atom per cent of Ce\(^{+++}\) in the Nd\(^{+++}\) spin system, however,
can probably be neglected. The amount of other paramagnetic impurities except Ce will be even more negligible. It was therefore decided to be content with only 99% pure Nd salt.

d) Crystallographical and Optical Requirements of the Crystal

The crystal should be so small that $Q_u$ stays high, violent perturbations of the cavity are avoided, and the number of atomic dipoles is small enough to allow an easy saturation of the spin-system.

The shape should be such as to allow the light beam to pass the magnetic dipoles in series rather than in parallel. This can be achieved by growing a crystal which is thin in diameter and long in the direction of the optical axis. The longer the crystal the larger the Faraday rotation will be, and the smaller the diameter of the crystal the easier the spin-system can be saturated. A crystal of about 1.5 mm length and 1.5 mm diameter has $N = 1.6 \cdot 10^{19}$ magnetic dipoles, a tolerable number for the requirement of power saturation. The crystal cannot be chosen thinner because of the difficulty of adjusting the light beam which sometimes has to be done after the liquid helium transfer and the alignment of the cavity resonator and the dewars in the magnetic field.

The length of the crystal cannot be chosen larger than 4 mm because of the size of the choke plunger to which the crystal will be attached and the geometry of the microwave field in the cavity.
The crystal has to be furnished with two plane parallel faces one on the front and one on the back, about 2 to 3 mm apart, perpendicular to the c-axis, the optic axis.

The crystal should be adjusted such that the light enters parallel to the optical axis and perpendicular to the two plane parallel faces. Since the crystal is dicroitic and double refractive, any deviation from this direction will result in elliptically polarised light. This can happen if the light beam, the optic axis of the crystal and the direction of the magnetic field are not parallel to each other, or if the two plane parallel faces are not perpendicular to the optic axis. When the paramagnetic resonance is only slightly saturated, the corresponding change of the paramagnetic Faraday effect can hardly be detected with elliptically polarised light.

When the crystal contains flaws and pockets which scatter light in unwanted directions then the crystal will always appear dim between crossed nicols.

The clearness of extinction also depends on the received light intensity and is better for a more intense light source. The most intense light in the visible region which is easily available in this physics laboratory is the green line \( \lambda = 5461 \) Å of a mercury arc.

The light coming from an a.c. mercury discharge has to pass about 2 m of air, 8 pyrex glass walls, twice through liquid nitrogen and twice through liquid helium, the crystal under question, two glass lenses, two nicol prisms and various
FIGURE 18

OPTICAL SET-UP for the FARADAY EFFECT
focussing devices attached to the nicols, three glass filters
the purpose of which is to select the above-mentioned wave length.

6.6) The Experimental Set-up

The requirements for carrying out the experiment in
question were outlined in previous sections. It has been shown
that the necessary power level for the saturation of the
resonance can easily be obtained, because of the high power
output of the klystron and the high Q of the cavity resonator.
As described in chapter III the cavity is provided with windows
to let the light through. For the same reason the silver layer
of a part of the dewars was removed. As intense monocromatic
light the green line (λ = 5461 Å) was chosen. It was obtained
from a General Electric AC arc and filters. It was then passed
through a nicol prism polariser, through the hollow poles of the
electromagnet, through the cavity, out through the magnet, and
finally through a nicol prism analyser. The emergent light was
condensed on to the cathode of a photomultiplier 1P21 and the
anode current was taken as a measure of the light passing through
the system. The details of the optics system are given in the
figure.

The light passed along the optic axis of the neodymium
ethylsulphate crystal and the path length was 1.6 mm.

The fact that the slightest deviation of the optic
axis from the direction of the light beam generates ellipticity
in the polarisation of the light was used for the alignment of
the crystal. The analysing nicol was rotated until the photomultiplier current was a minimum. Then the crystal was slightly rotated in the cavity by turning the crystal holder until the minimum could not be improved any more. A rotational adjustment of the crystal about an axis perpendicular to the other one was not possible. The crystal, however, was pressed with a face that is parallel to the optic axis on to the surface of the plunger which is in turn designed to be parallel to the external magnetic field and parallel to the light beam. Here a deviation of about 1° can easily happen. The measured minimum was indeed broad which is the reason of the low accuracy in the angle measurements.

6.7) Preparation of the Crystal

a) The Chemistry

The ethylsulphate of neodymium \( \text{Nd}(C_2H_5SO_4)_3 \cdot 9H_2O \), used in this investigation, was prepared from equivalent portions of analytically pure barium ethylsulphate \( \text{Ba}(C_2H_5SO_4)_2 \cdot 2H_2O \) and neodymium sulphate \( \text{Nd}_2(SO_4)_3 \cdot 8H_2O \), which in turn was prepared from 99% chemically pure \( \text{Nd}_2O_3 \) (supplied by Lindsay Chemical Co.) and an equivalent amount of chemically pure sulfuric acid. \( \text{Nd}_2(SO_4)_3 \cdot 8H_2O \) was recrystallised several times and washed with distilled water at room temperature until the solution was quite neutral.

The solutions of barium ethylsulphate and neodymium sulphate were brought to crystallisation by concentrating in a
vacuum desiccator containing silica gel at room temperature, after removing the barium sulphate by decantation and several successive filtrations through finest filter paper. Barium sulphate is almost colloidal and is difficult to remove. To avoid decomposition of the \( \text{(C}_2\text{H}_5\text{SO}_4) \)-bond careful attention was paid to let neither the solution nor the finally obtained crystals warm up above room temperature.

b) Growing the Crystal

The rare earth ethylsulphates grow in hexagonal dipyramidal prisms. In most cases neodymium ethylsulphate crystals grew in plates of which the two large opposite faces are parallel to the c-axis (Fig. 19). The crystal structure has been determined by Jaeger and Ketelaar to be of \( \text{C}_{3h} \) symmetry.

After several attempts to grow crystals in a small beaker, which did not result in useful material, seeds were suspended from the surface of just saturated solutions. Within a week well-shaped crystals were obtained. It was found that the solutions had to be extremely clear, free from dust and remaining particles. The optical properties, however, were bad. Some of the crystals contained milky clouds of unknown origin, others had air bubbles or flaws. Investigation of the crystals with a polarisation microscope showed that some were twinned inside and had to be rejected. A small crystal which did not look too good from the optical viewpoint was finally used for
the experiments as I was not able to continue the efforts in crystal growing because of lack of time.

Tests were made to see whether the crystals could stand vacuum, since they were to be used in a sealed cavity under vacuum for a paramagnetic resonance experiment necessary to determine $g_H$ before the experiments on the Faraday effect could be done.

It was found that the crystal loses water of crystallization somewhat below a pressure of 1 mm Hg. At $10^{-2}$ mm Hg the crystal turns into a powder within two hours.

All good neodymium ethylsulphate material was kept in a refrigerator to avoid decomposition of the $(\text{C}_2\text{H}_5\text{SO}_4)$-group.

c) Cutting of Two Plane Parallel and Polished Faces

Perpendicular to the Optic Axis

For grinding and polishing the crystal perpendicular to the optic axis, a special machine was designed. The idea was to let the crystal rest in a metal groove on two of its neighbouring large hexagonal faces which make an outside angle of $120^\circ$ then clamp and tie it in this position.

The apparatus consists of a circular brass rod sliding without play in a boring of a large steel block whose surface is plane and perpendicular ($\pm 0.1^\circ$) to the axis of the boring. Both parts are made on a lathe and a deviation from $90^\circ$ less than $0.2^\circ$ was guaranteed.

At the end of the rod a groove having two faces which
make an angle of $120^\circ \pm 0.3^\circ$ and which are parallel to the rod axis was cut as accurately as it could be done on a milling machine.

The rod was also furnished with assemblies for holding the crystal in place; a platform as support for the bottom end of the crystal, and holes in the faces of the groove and cleats are provided for the silk threads (see picture). The rod could be fixed in any position within the boring by means of two set-screws one from underneath and one from the side. After the crystal has been mounted, the rod was lowered until the surface of the steel block and the top of the brass rod were flush.

Grinding was done with several abrasives in the following sequence: a) emery paper 3/0, b) emery paper 4/0, c) fine blotting paper, and d) chamois leather.

6.8) Experimental Results

a) Paramagnetic Resonance of Nd$^{+++}$ in Nd(C$_2$H$_5$SO$_4$)$_2 \cdot 9$H$_2$O:

Determination of $g_{\|}$

The crystal under investigation was mounted as usual on the choke plunger in the cavity. It rests with one hexagonal side face on the plunger while the opposite hexagonal face was pressed by a teflon arc. The optic axis is parallel to the surface of the plunger and consequently parallel to the bottom of the cavity. The cavity was evacuated and then filled with helium gas to a pressure just below atmospheric pressure.

$g_{\|}$ was measured at 4.2$^\circ$K for the concentrated salt:
$g_H = 3.45 \pm 0.05$. This compares with Scovil's value of 3.535 for the diluted salt at $20^\circ K$.

The experiments on the Faraday effect (see next section) show that at $1.4^\circ K$ the centre of the paramagnetic resonance curve lies at about $H = 1.75$ kOe which would give a splitting factor $g_H = 3.7$.

b) Measurements of the Paramagnetic Faraday Rotation when Microwave Power Is Applied

In order to obtain a large Faraday rotation the experiments were all carried out at temperatures as low as could possibly be obtained with the apparatus.

The helium vapour was pumped off by means of a large rotary pump. The pumping speed could be varied by adjustment of three stopcocks in parallel; a large one, a medium sized one, and a small one. The temperature which was measured with a vapour pressure manometer (filled with Apiezon oil B), could be kept constant within $0.01^\circ K$ over several hours. Thus a temperature of $1.39^\circ K$ could be maintained for several hours.

The magnetic field and the frequency were measured as usual in standard paramagnetic resonance technique.

The microwave power level was found very constant, after the klystron had been in operation for one hour.

For each point of the Faraday curve a series of ten measurements has been taken. To obtain a better average, half of the measurements were taken by approaching the minimum photo
Figure 20

A Low power.
B Medium power.
C High power.
electric current setting from one side, half of them from the other side. The average error of the readings was $\pm 0.5^\circ$ with occasional deviations as large as $1^\circ$. Measurements were taken at different microwave power levels, as indicated in the figure. The angle of rotation of the plane of polarisation is plotted as a function of magnetic field for four cases: No microwave power, high microwave power, medium microwave power, and a low value of power. When no microwave power is applied the measured Faraday curve checks with the previous measurements of Becquerel et al. $^{11}$ within 2%. Finally, the effect which was predicted by A. Kastler has been established.

The line shape of the measured curves $A$ and $B$ should have triplet structure due to spin-spin interaction $^7$. This has not been resolved.

c) Estimation of the Applied Power Level and the Amplitude of the Microwave Field

The exact value of the power level and the amplitude of the field have not been determined. It was tried, however, to estimate the order of magnitude. For this purpose the transmitted power of the cavity resonator was used for all the information. The output coupling of the cavity resonator was deliberately made very small just to obtain an indication whether the klystron was tuned to the resonance frequency of the cavity.

Since the transmitted power out of the cavity is a strictly linear function of the power coupled into the cavity
only, the detected transmitted power can be used for comparison of power levels. Torrey and Whitmer (1948) and Beringer (1944) have measured characteristics of silicon tungsten rectifiers. Below a power level of \(10 \mu W\) the silicon tungsten rectifiers obey rigorously the square law in its response. Above this power level the characteristic is more or less linear. Measurements are also made in this region by Beringer as continuation of Torrey and Whitmer's investigations. Such a silicon tungsten rectifier is the 1N23B. When its power level at one point is known an extrapolation of the power level down to lower values of the current can be made, which will give a good estimate.

At a fairly high power level the amount of power dissipated in the cavity was determined calorimetric at \(4.2^\circ K\) by comparison of the two evaporation rates of liquid helium when power is applied and when power is switched off.

When the rectified current of the receiving 1N23B crystal was \(320 \mu A\) (the d.c. impedance of the crystal being large in comparison with the resistance of the microammeter) the power dissipated in the walls and the dielectric material of the cavity resonator is \(140 \text{ mW}\) with an error less than 10%.

Since the transmission line is critically coupled to the cavity resonator it can be assumed that the loss in the coaxial line is small in comparison with \(140 \text{ mW}\), and may be included in the error. Thus we take \(P_L = 140 \text{ mW} \pm 10\%\). \(P_L\) approximately equals the power input to the cavity because
### Table 8

<table>
<thead>
<tr>
<th>Curve</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage saturation</td>
<td>52%</td>
<td>88%</td>
<td>100%</td>
</tr>
<tr>
<td>$T$ in $^\circ K$</td>
<td>1.39</td>
<td>1.39</td>
<td>1.59</td>
</tr>
<tr>
<td>Current through 1N23B</td>
<td>$(0.85 \pm 0.10)10^{-2}$ $\mu A$</td>
<td>$(3.5 \pm 0.1)10^{-2}$ $\mu A$</td>
<td>$(320 \pm 5)$ $\mu A$</td>
</tr>
<tr>
<td>Power level on 1N23B</td>
<td>$(0.033 \pm 0.004)$ $\mu W$</td>
<td>$(0.117 \pm 0.004)$ $\mu W$</td>
<td>$(360 \pm 5)$ $\mu W$</td>
</tr>
<tr>
<td>Power dissipated in cavity $P_L$</td>
<td>$(13 \pm 3)$ $\mu W$</td>
<td>$(46 \pm 5)$ $\mu W$</td>
<td>$(0.14 \pm 0.01)$ $W$</td>
</tr>
<tr>
<td>Peak value of stored energy $W$</td>
<td>$(21\pm5)10^{-13}$ Joule</td>
<td>$(73\pm8)10^{-13}$ Joule</td>
<td>$(2.23\pm0.16)10^{-8}$ Joule</td>
</tr>
<tr>
<td>Square of the amplitude of the microwave field $\mathbf{H}$</td>
<td>$(1.37\pm0.33)(A/m)^2$</td>
<td>$(4.75\pm0.5)(A/m)^2$</td>
<td>$(1.45\pm0.1)10^4$ $(A/m)^2$</td>
</tr>
<tr>
<td>Power dissipated in sample $P_S$</td>
<td>$(22 \pm 5.5)$ $\mu W$</td>
<td>$(33 \pm 4)$ $\mu W$</td>
<td>$(42 \pm 3)$ $\mu W$</td>
</tr>
<tr>
<td>Power input to cavity</td>
<td>$(35 \pm 9)$ $\mu W$</td>
<td>$(79 \pm 9)$ $\mu W$</td>
<td>$(0.14 \pm 0.01)$ $W$</td>
</tr>
<tr>
<td>Calculated $\tau_L$</td>
<td>$\frac{1}{25}$ s</td>
<td>$\frac{1}{12}$ s</td>
<td>---</td>
</tr>
</tbody>
</table>
the dissipated power in the sample is much smaller than $P_L$ according to equations (15) and (16), and reflection and transmission can be neglected in this estimation. From $P_L$ using the formula (16) $\hat{W}$ and then the amplitude $\hat{H}$ at the point of the sample have been calculated. $\hat{H}$ follows from (17) and (18).

The applied microwave power and the amplitude $\hat{H}$ for the three curves $A$, $B$ and $C$ in Fig. 20 are given in Table 8.

The power dissipated in the sample cannot be calculated before an estimate of the spin-lattice relaxation has been made. This will be done in the next section.

d) Estimation of the Electron Spin-Lattice Relaxation Time

From curve A (showing about 50% saturation) and curve B (showing about 88% saturation) we can obtain a fair approximation of $\tau_L$. We introduce in equation (7) for $\tau_L$ the modified expression $(\tau_L \cdot \tau_s)^{-\frac{1}{2}}$ as it was done in equation (11). Then we obtain for 50% saturation

$$\frac{\Delta \rho}{\rho} = \frac{1}{2} = \frac{1}{1 + \left[ \frac{\mu_1 \hat{H}}{k (\tau_L \tau_s)^{-\frac{1}{2}}} \right]^2} \quad \text{or} \quad \left( \frac{\mu_1}{\tau_L} \right)^2 \hat{H} \tau_L \tau_s = 1$$

and for 88% saturation

$$\frac{\Delta \rho}{\rho} = 0.888 \quad \text{or} \quad \left( \frac{\mu_1}{\tau_L} \right)^2 \hat{H} \tau_L \tau_s = 7.35$$

From both curves the same order of magnitude is obtained, namely

$$\tau_L \approx \frac{1}{20} \text{ s}.$$
Thus the electron spin-lattice relaxation time for Nd$^{+++}$ at 1.5°K is approximately $\frac{1}{20}$ s.

With this approximate value of $\tau_L$, $P_z$ has been calculated using formula (16); its values are shown in table 8.

c) The Temperature Dependence of the Saturation

Since the electron spin-lattice time is temperature dependent, it was tried to measure the saturation in the Faraday curve as a function of the temperature in the range from 1.3°K to 2.18°K.

Unfortunately, the crystal with which the results were obtained had started to decompose. A fine cloud had developed inside which made it impossible to extinguish the light between crossed nicols because of the diffuse scattering of the light. Another crystal which was twinned inside was tried without success after the twinned half was cut away and the sides covered with plasticine.

6.9) Future Experiments

The completed experiments and obtained results suggest a series of other interesting experiments. First of all, the so far developed technique should be improved in particular the optic system such that the error of the rotation angle measurements is decreased to, say, at least $\frac{1}{10}$°. The
following investigations are suggested:

1) It should be tried to measure the fine structure in the saturation curve of Nd(C$_2$H$_5$SO$_4$)$_3$.9H$_2$O, which has triplet structure due to spin-spin interaction. In general, the saturation of the Faraday effect enables and facilitates to measure the line shapes of paramagnetic resonance absorption signals in case of concentrated salts.

2) The temperature dependence of the saturation should be measured by varying the pumping speed and keeping the power level constant. From this experiment the temperature dependence of the electron spin-lattice relaxation time could be derived.

3) Since the electron spin-lattice relaxation time $\tau_L$ of Nd$^{+++}$ in Nd(C$_2$H$_5$SO$_4$)$_3$.9H$_2$O is fairly long ($\frac{1}{20}$ s) an a.c. method could detect it directly. The potential of the klystron reflector could be modulated with square waves with varying frequencies and the rotation either observed directly or from the varying photoelectric current which, in turn, can be transformed into a voltage and displayed on a cathode ray oscilloscope.

4) Other rare earth salts (having a large Faraday rotation) should be investigated even in diluted forms in order to detect the absorption curves in case of multiplets.

5) If 4) works, the lattice relaxation of various energy levels in solid state MASERs should be investigated using the methods mentioned above.
6.10) References

1) Kastler, A., Compt. rend. 232 (1951), 953
2) Opechowski, W., Rev. Mod. Phys. 25 (1953), 264
3) Bloembergen, N., Purcell, E.M., Pound, R.V.,
   Phys. Rev. 73 (1948), 679
4) Bleaney, B., Scovil, H.E.D., Trenam, R.S.,
5) Roberts, L.D., Sartain, C.C., Borie, B.,
   Rev. Mod. Phys. 25 (1953), 170
   16 (1953), 108
7) Bleaney, B., Elliott, R.J., Scovil, H.E.D.,
   Proc. Phys. Soc. A64 (1951), 933
8) Feher, G., Scovil, H.E.D., Phys. Rev. 105 (1957), 761
9) Jaeger, M.F.M., Recueil des travaux chemiques 33 (1914), 342
11) Becquerel, J., De Haas, A., van den Handel, J.,
    Physica 5 (1938), 753
12) Torrey, H.C., Whitmer, C.A., Crystal Rectifiers, vol. 15,
    Radiation Laboratory Series, pp. 333-335

Beringer, E.R., see p. 334
A.1) Notes on Silver Plating of a Cavity Resonator

For the cleaning and silver plating the instructions of the "Tube Laboratory Manual", published by the Massachusetts Institute of Technology, have been followed.

The silver-plated surface was ball burnished with stainless steel tools of pencil shape whose ends were formed to smooth ball points of various diameters.

The procedure of electrolytic polishing of silver is described in Shuttleworth, King, Chalmers, Metal Treatment 51(1947), 161.

Any residual film of the polished silver surface has to be carefully removed with distilled water in order to guarantee a high Q of the cavity.

A.2) Indium-Glass-Brass Seals

The problem to obtain a vacuum tight glass to brass seal at liquid helium temperatures is easily solved by means of an indium O-ring. When both the glass and the brass surfaces are clean, clean indium sticks to them as if the glass surface were "glued" to the metal. The O-rings are formed by compression of an almost ring shaped indium ingot into a mould. The mould consists of two forms which when pressed together, cut the O-ring out of the ingot. It is necessary to lubricate the mould with oil in order to avoid the soldering action between the two metals.