The University of British Columbia
Faculty of Graduate Studies

PROGRAMME OF THE

FINAL ORAL EXAMINATION
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

of

LLOYD BURDETT ROBINSON
B. A. (Saskatchewan) 1953
M. A. (Saskatchewan) 1954

MONDAY, JULY 29th, 1957, at 10:30 a.m.

IN ROOM 300, PHYSICS BUILDING

COMMITTEE IN CHARGE
DEAN G. M. SHRUM, Chairman

M. BLOOM
A. M. CROOKER
J. M. DANIELS
J. B. GUNN

F. M. C. GOODSPEED
H. G. HEAL
A. D. MOORE
V. J. OKULITCH

External Examiner: H. E. PETCH
McMaster University
THE NUCLEAR SPIN RESONANCE SPECTRUM
OF AL$^{27}$ IN SPODUMENE

ABSTRACT

Using the techniques of radio-frequency resonance spectroscopy, experimental studies of the nuclear spin resonance spectrum of Al$^{27}$ in single crystals of spodumene (LiAl(SiO$_3$)$_2$) have been carried out over a wide range of externally applied magnetic field.

In spodumene, interactions of the magnetic dipole moment with an external magnetic field, and also interactions of the electric quadrupole moment with the crystalline electrostatic field, gradient can affect the energies of Al$^{27}$ nuclei. We define $R$ as the ratio of magnetic to electrostatic interaction energies. The object of this work has been to measure experimentally a nuclear resonance spectrum over a wide enough range of magnetic field to link the regions where $R$ is much greater than or much less than unity. Much experimental data is available in the literature for crystals where $R$ differs appreciably from unity, but no experimental results have been given before for the intermediate region where $R$ is of the order of unity and where the spectrum is more complex.

Using data obtained from high field measurements in spodumene by Petch and Cranna, Lamarche has calculated energy levels by exact diagonalization of the Hamiltonian over a wide range of $R$ values for a particular orientation of the spodumene crystal in a magnetic field. Calculations for other orientations have been made using electronic computers at the University of Toronto and at the University of British Columbia.

Several of the predicted resonances have been observed. One transition has been observed over a range of magnetic field covering the region from $R$ much less than unity to $R$ much greater than unity. Resonance frequencies observed have been in good agreement with calculated transition frequencies.

A new method of using a knowledge of the spin eigenstates to predict signal voltage for an induction spectrometer has been checked at values for $R$ of the order of unity. It gives good agreement with experimental signal voltage measurements.

Pure quadrupole transitions have been observed in spodumene at 751.5 kc and 793.5 kc with an estimated probable error of 2 kc, using an induction spectrometer with Zeeman modulation. These measurements are the lowest frequency pure quadrupole resonances reported to date.
Measurements of Gamma-ray Absorption in Carbon

R. N. H. Haslam, R. J. Horsley, H. E. Johns, and L. B. Robinson
Canadian Journal of Physics 31, 636. (1953)

Fine Structure of the gamma neutron Activation Curve in Fluorine

J. V. G. Taylor, L. B. Robinson, and R. N. H. Haslam
Canadian Journal of Physics 32, 238. (1954)
GRADUATE STUDIES

Field of Study: Physics

Electromagnetic Theory .......................... J. R. H. Dempster
Nuclear Physics .................................. K. C. Mann
Quantum Mechanics ............................. G. M. Volkof.
Noise in Physical Systems ....................... R. E. Burgess
Advanced Electronics ............................ R. E. Burgess

Other Studies:

Network Theory .................................. A. D. Moore
Servomechanisms ................................. E. V. Bohn
Numerical Analysis .............................. F. M. C. Goodspeed
THE NUCLEAR SPIN RESONANCE SPECTRUM
OF Al$^{27}$ IN SPODUMENE

by

LLOYD BURDETT ROBINSON

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
PHYSICS

We accept this thesis as conforming to the standard
required from candidates for the degree of
DOCTOR OF PHILOSOPHY

THE UNIVERSITY OF BRITISH COLUMBIA
July 1957
Using the techniques of radio-frequency resonance spectroscopy, experimental studies of the nuclear spin resonance spectrum of \(^{27}\)Al in single crystals of spodumene (LiAl(SiO\(_3\))\(_2\)) have been carried out over a wide range of externally applied magnetic field.

In spodumene, interactions of the magnetic dipole moment with an external magnetic field, and also interactions of the electric quadrupole moment with the crystalline electrostatic field gradient can affect the energies of \(^{27}\)Al nuclei. We define \(R\) as the ratio of magnetic to electrostatic interaction energies. The object of this thesis has been to measure experimentally a nuclear resonance spectrum over a wide enough range of magnetic field to link the regions where \(R\) is much greater than or much less than unity. Much experimental data is available in the literature for crystals where \(R\) differs appreciably from unity, but no experimental results have been given before for the intermediate region where \(R\) is of the order of unity and where the spectrum is more complex.

Using data obtained from high field measurements in spodumene by Petch and Cranna, Lamarche has calculated energy levels by exact diagonalization of the Hamiltonian over a wide range of \(R\) values for a particular orientation of the spodumene crystal in a
magnetic field. Calculations for other orientations have been made using electronic computers at the University of Toronto and at the University of British Columbia.

Several of the predicted resonances have been observed. One transition has been observed over a range of magnetic field covering the region from $R$ much less than unity to $R$ much greater than unity. Resonance frequencies observed have been in good agreement with calculated transition frequencies.

A new method of using a knowledge of the spin eigenstates to predict signal voltage for an induction spectrometer has been checked at values for $R$ of the order of unity. It gives good agreement with experimental signal voltage measurements.

Pure quadrupole transitions have been observed in spodumene at 751.5 kc and 793.5 kc with an estimated probable error of 2 kc, using an induction spectrometer with Zeeman modulation. These measurements are the lowest frequency pure quadrupole resonances reported to date.
GRADUATE STUDIES

Field of Study: Physics

Electromagnetic Theory ........................................ J. R. H. Dempster
Nuclear Physics .................................................. K. C. Mann
Quantum Mechanics .............................................. G. M. Volkoff
Noise in Physical Systems ..................................... R. E. Burgess
Advanced Electronics ........................................... R. E. Burgess

Other Studies:

Network Theory .................................................. A. D. Moore
Servomechanisms ............................................... E. V. Bohn
Numerical Analysis ............................................. F. M. C. Goodspeed

The University of British Columbia
Faculty of Graduate Studies

PROGRAMME OF THE

FINAL ORAL EXAMINATION

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

of

LLOYD BURDETT ROBINSON
B. A. (Saskatchewan) 1953
M. A. (Saskatchewan) 1954

MONDAY, JULY 29th, 1957, at 10:30 a.m.

IN ROOM 300, PHYSICS BUILDING

COMMITTEE IN CHARGE

DEAN G. M. SHRUM, Chairman
M. BLOOM F. M. C. GOODSPEED
A. M. CROOKER H. G. HEAL
J. M. DANIELS A. D. MOORE
J. B. GUNN V. J. OKULITCH

External Examiner: H. E. PETCH
McMaster University
THE NUCLEAR SPIN RESONANCE SPECTRUM
OF AL$^{27}$ IN SPODUMENE

Abstract

Using the techniques of radio-frequency resonance spectroscopy, experimental studies of the nuclear spin resonance spectrum of Al$^{27}$ in single crystals of spodumene (LiAl(SiO$_3$)$_2$) have been carried out over a wide range of externally applied magnetic field.

In spodumene, interactions of the magnetic dipole moment with an external magnetic field, and also interactions of the electric quadrupole moment with the crystalline electrostatic field gradient can affect the energies of Al$^{27}$ nuclei. We define \( R \) as the ratio of magnetic to electrostatic interaction energies. The object of this work has been to measure experimentally a nuclear resonance spectrum over a wide enough range of magnetic field to link the regions where \( R \) is much greater than or much less than unity. Much experimental data is available in the literature for crystals where \( R \) differs appreciably from unity, but no experimental results have been given before for the intermediate region where \( R \) is of the order of unity and where the spectrum is more complex.

Using data obtained from high field measurements in spodumene by Petch and Cranna, Lamarche has calculated energy levels by exact diagonalization of the Hamiltonian over a wide range of \( R \) values for a particular orientation of the spodumene crystal in a magnetic field. Calculations for other orientations have been made using electronic computers at the University of Toronto and at the University of British Columbia.

Several of the predicted resonances have been observed. One transition has been observed over a range of magnetic field covering the region from \( R \) much less than unity to \( R \) much greater than unity. Resonance frequencies observed have been in good agreement with calculated transition frequencies.

A new method of using a knowledge of the spin eigenstates to predict signal voltage for an induction spectrometer has been checked at values for \( R \) of the order of unity. It gives good agreement with experimental signal voltage measurements.

Pure quadrupole transitions have been observed in spodumene at 751.5 kc and 793.5 kc with an estimated probable error of 2 kc, using an induction spectrometer with Zeeman modulation. These measurements are the lowest frequency pure quadrupole resonances reported to date.

Publications

Measurements of Gamma-ray Absorption in Carbon
R. N. H. Haslam, R. J. Horsley, H. E. Johns, and L. B. Robinson
Canadian Journal of Physics 31, 636. (1953)

Fine Structure of the gamma neutron Activation Curve in Fluorine
J. V. G. Taylor, L. B. Robinson, and R. N. H. Haslam
Canadian Journal of Physics 32, 238. (1954)
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.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS

ABSTRACT

CHAPTER I - INTRODUCTION

CHAPTER II - THEORY

A. Energy Levels
   1. The Hamiltonian 5
   2. Solution of the Hamiltonian for \( \theta = 0 \) 11
   3. Solution of the Hamiltonian for \( \theta \neq 0 \) 12

B. Transition Probabilities and Signal Intensities 14

C. Signal to Noise Ratio 18

D. Choice of Crystal for the Experiment 21

CHAPTER III - EXPERIMENTAL APPARATUS

A. Description of Samples 24

B. Choice of Spectrometer 26

C. The Nuclear Induction Spectrometer
   1. General Design 29
   2. Pure Quadrupole Induction Spectrometer 33
   3. The Magnet 34

D. Difficulties 37

CHAPTER IV - EXPERIMENTAL PROCEDURE 41

CHAPTER V - EXPERIMENTAL RESULTS

A. Resonance Frequencies
   1. Interfering Resonances 45
   2. Al\(^{27}\) Resonances for \( \theta = 0 \) 46
   3. Al\(^{27}\) Resonances for \( \theta \neq 0 \) 49
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. Signal Intensities</td>
<td>51</td>
</tr>
<tr>
<td>C. Pure Quadrupole Measurements and Numerical Values for Quadrupole Coupling Constants</td>
<td>53</td>
</tr>
<tr>
<td>CHAPTER VI - DISCUSSION</td>
<td>57</td>
</tr>
<tr>
<td>APPENDIX A - Phenomenological Equations for a Two Level System</td>
<td>64</td>
</tr>
<tr>
<td>APPENDIX B - Notes on Diagonalization of Matrices</td>
<td>67</td>
</tr>
<tr>
<td>APPENDIX C - Experiments on Bridge Type Spectrometers</td>
<td>70</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>72</td>
</tr>
<tr>
<td>TABLE I - Comparison of Results Obtained for ( \eta ) and ( e^2qQ ) at Different Values of ( R ).</td>
<td>56</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>FIG.</th>
<th>DESCRIPTION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 1</td>
<td>Energy Levels for $\theta = 0^\circ$</td>
<td>11</td>
</tr>
<tr>
<td>Fig. 2</td>
<td>Transition Frequencies for $\theta = 0^\circ$</td>
<td>11</td>
</tr>
<tr>
<td>Fig. 3</td>
<td>Energy Levels for $\theta = 10^\circ$</td>
<td>13</td>
</tr>
<tr>
<td>Fig. 4</td>
<td>Theoretical Variation of Signal Voltage as a Function of $R$</td>
<td>18</td>
</tr>
<tr>
<td>Fig. 5</td>
<td>Circuit Diagram for Induction Spectrometer</td>
<td>30</td>
</tr>
<tr>
<td>Fig. 6</td>
<td>Block Diagram of Experimental Apparatus</td>
<td>37</td>
</tr>
<tr>
<td>Fig. 7</td>
<td>Resonance Spectrum for $\theta = 0$</td>
<td>46</td>
</tr>
<tr>
<td>Fig. 8</td>
<td>Resonance Spectrum for $\theta = 5^\circ$</td>
<td>50</td>
</tr>
<tr>
<td>Fig. 9</td>
<td>Resonance Spectrum for $\theta = 10^\circ$, $\theta = 20^\circ$</td>
<td>50</td>
</tr>
</tbody>
</table>

PLATE 1 - Comparison of Records Obtained Under Identical Conditions  

<table>
<thead>
<tr>
<th>PLATE</th>
<th>DESCRIPTION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>Records of $\nu_2$, $\nu_7$; $\nu_4$, $\nu_6$</td>
<td>48</td>
</tr>
<tr>
<td>III</td>
<td>&quot;Splitting&quot; of $\nu_2$ at 800 kc.</td>
<td>49</td>
</tr>
<tr>
<td>IV</td>
<td>Records of Pure Quadrupole Resonances in Spodumene</td>
<td>54</td>
</tr>
<tr>
<td>V</td>
<td>A Record of Li$^7$ and Al$^{27}$ Resonances at 313 kc.</td>
<td>58</td>
</tr>
<tr>
<td>VI</td>
<td>Selected Runs to Demonstrate Good Signal to Noise Ratio</td>
<td>59</td>
</tr>
<tr>
<td>VII</td>
<td>A Record Obtained from the Solution of the Hamiltonian Matrix by the Computer Alwac III E</td>
<td>70</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

The work described in this thesis was supported by the National Research Council of Canada, by means of research grants to Professor G. M. Volkoff and by the award of two studentships to the author in the period 1955-57.

I should like to express my appreciation to Dr. Volkoff, who suggested this investigation. His advice and encouragement were largely responsible for its successful completion.

Dr. Bloom has been very generous with both his time and assistance, and in numerous conversations has contributed greatly to the author's understanding of this field of Physics.

I should also like to express my thanks to Miss Jayaseetha Rau, who assisted in many of the numerical calculations; to Mr. A. J. Frazer, Mr. W. Morrison and Mr. J. Lees for their co-operation in the construction of equipment.

This research has been greatly aided by the use of the electronic computers at the University of Toronto and at the University of British Columbia. The assistance and co-operation given by the staff associated with these machines is gratefully acknowledged.

Finally, I should like to express appreciation to my wife, who has helped both by her encouragement and by her assistance in preparing the draft of this thesis.
CHAPTER I

INTRODUCTION

In 1924 Pauli suggested that the atomic nucleus possesses a magnetic moment. It was also suggested that the magnetic moment is associated with an intrinsic angular momentum or "spin" of the nucleus. These ideas make it possible to understand the hyperfine splitting which occurs in atomic spectra. Quantum theory shows that the projection of total angular momentum on any axis can only give integral or half-integral multiples of $\frac{\hbar}{2\pi}$, where $\hbar$ is Planck's constant. Thus it is not possible to observe a continuous range of values of angular momentum, but only discrete ones, and only discrete values will be obtained for the projection of the magnetic moment of the nucleus along any axis. This leads to discrete values or levels for the energy due to the interaction of the nuclear magnetic moments with a magnetic field.

Direct evidence of the discrete orientations of magnetic moments was obtained for protons in 1933, by using the deflecting effect of an inhomogeneous magnetic field on the magnetic moment of the protons in a stream of hydrogen molecules (1). The beam of molecules divided into three, indicating three possible values of the total magnetic moment of the two protons present in each molecule. The discreteness of the energy levels in a magnetic field was shown directly in 1937, by causing transitions between levels by use of a radio-frequency magnetic field (2).
When transitions occurred, a change in the number of molecules in one of the beams was observed.

The magnetic moment of nuclei should lead to a weak paramagnetic effect. The paramagnetism was first observed in 1937 in solid hydrogen (3). This observation showed that the effects of the nuclear magnetic moment could be observed in bulk material as well as in molecular beams.

It was pointed out by Gorter (4) in 1936 that in principle at least, transitions between the nuclear magnetic energy levels should be observable in bulk material. In 1946, two groups, working independently, succeeded in observing the transitions between nuclear magnetic energy levels.Bloch, Hansen and Packard (5) measured induction signals from transitions between proton levels in water, while Purcell, Torrey and Pound (6) detected the absorption of energy from a resonant electronic circuit by proton transitions in paraffin wax.

The energy difference between nuclear magnetic energy levels is such that transitions between the levels give rise to radiation in the radio-frequency range for magnetic fields obtainable in the laboratory. The branch of radio-frequency spectroscopy dealing with such transitions is called Nuclear Magnetic Resonance, often abbreviated to NMR.

Atomic spectroscopy led to another piece of information about the nucleus. Deviations from an interval rule in the spectrum of Europium, observed in 1935, were explained by Casimir (7), who suggested that the nucleus had a non-spherical charge distribution which would lead to
a quadrupole moment. The interaction of the nucleus with the electrostatic field gradient produced by the surrounding electron cloud is different for different orientations of the nucleus. This effect perturbs the electronic energy levels; it also leads to a change in the energy levels of the nucleus.

In many nuclear magnetic resonance experiments the electrostatic field gradient averages out to zero, so that the quadrupole effect can be neglected so far as the energy levels are concerned. However, in the case of some molecules, and in crystals, it is possible for a nucleus to be placed at a position where the electrostatic field gradient does not average to zero, and the resulting interaction will change the energy levels of the nucleus.

In 1948 Bloembergen (8) reported effects of quadrupole interactions with the deuteron. Pound (9) found nuclear magnetic resonances which were split into several lines by the quadrupole interaction in single crystals.

In 1951 Dehmelt and Kruger (10) found resonances due to transitions between nuclear quadrupole energy levels, using the techniques of nuclear magnetic resonance but with no applied magnetic field. This is termed Nuclear Quadrupole Resonance, sometimes abbreviated to NQR.

In the six years which have elapsed since pure quadrupole resonances were first observed, many experiments have been performed to study various aspects of quadrupole and magnetic interactions of nuclei. Observations have been made of pure quadrupole resonances for many nuclei in a variety of materials. The perturbing effect of a small magnetic interaction on a large quadrupole interaction has been studied, and the effect
of a small quadrupole interaction on a large magnetic interaction has also
been observed. Wertz (11) has used the name Nuclear Spin Resonance to
point out the essential characteristic of these transitions and this term will
be used in the rest of the thesis.

Up to the present time, no experiment has been reported where
a transition has been observed over a sufficient range of magnetic fields to
permit a study of the gradual change from a quadrupole interaction perturbed
by a magnetic interaction, to a magnetic interaction perturbed by a quadrupole
interaction. This thesis describes an experiment where transitions were
observed between levels of the aluminum nucleus in a crystal of spodumene,
from zero and low magnetic field where the quadrupole interaction is dominant,
through the intermediate field region where electric quadrupole and magnetic
dipole interaction energies are of the same order, and up to higher fields
where the magnetic interaction is most important.

The emphasis in this study is not on the investigations of the
properties of the spodumene crystal or of the aluminum nucleus. The work
was done rather to provide the first example in the literature on Nuclear
Spin Resonance of a radio-frequency spectrum which covers a complete
range of ratios of the magnitudes of electric quadrupole and nuclear dipole
interactions to which a nucleus is subjected. Particular attention is paid
to the transition region not previously investigated elsewhere, in which
this ratio is close to unity, and in which the observed spectrum exhibits
certain characteristic differences from the previously studied limiting cases
where the ratio is either much greater than or much less than unity.
In any branch of spectroscopy, the observation of transitions between discrete energy levels is of primary interest. While in most branches of spectroscopy, many effects determine the values of the energy levels, and numerical predictions of the energy levels may be very difficult or impossible, in radio-frequency spectroscopy the energy levels are often due to only a few interactions and their values may be calculated using quite simple ideas.

The energy levels of an isolated nucleus in a magnetic field are known in terms of the magnetic field, and the spin and magnetic moment of the nucleus. They are given by \( E_m = m \frac{\mu H_0}{I} \) where the spin \( I \) is given in units of \( \hbar \), \( m \) gives the magnetic substate, taking on integral or half integral values in unit steps from \(-I\) to \(I\). If the magnetic field \( H_0 \) is in gauss, and if the magnetic dipole moment \( \mu \) is in c.g.s. units, \( E \) is in ergs.

The energy levels of a nucleus whose energy is due only to quadrupole interactions may also be written down immediately if the electrostatic gradient is axially symmetrical, and the axis of quantization is also
the axis of symmetry. The energy levels are given by

\[ E_m = \frac{e^2 qQ(3m^2 - I^2)}{4I(2I - 1)} \]

eq is the value of the electrostatic field gradient along the axis of symmetry, and \( eQ \) is the electric quadrupole moment of the nucleus. If, however, the electrostatic field gradient is not axially symmetrical, the Hamiltonian \( \mathcal{H}_Q \) of the system is more complex. In this case if the Hamiltonian is referred to the principal axes \( x, y, z \), of the electrostatic field gradient tensor defined in reference (12), then

\[ \mathcal{H}_Q = \frac{e^2 qQ}{4I(2I - 1)} \left( 3I_z^2 - I^2 + \eta (I_x^2 - I_y^2) \right) \]

where \( \eta \) is the asymmetry parameter of the above tensor, defined by

\[ \eta = \frac{\partial^2 \Phi/\partial x^2 - \partial^2 \Phi/\partial y^2}{\partial^2 \Phi/\partial z^2} \]

and \( \Phi \) is the electrostatic potential. \( I_x, I_y \) and \( I_z \) are the spin angular momentum operators. The terms in \( I_x^2 \) and \( I_y^2 \) lead to non-zero values for the elements \( \mathcal{H}_m, m \geq 2 \) of the Hamiltonian in the representation which diagonalizes \( I_z \) and so to find the energy levels we must diagonalize the Hamiltonian. Fortunately, it turns out that for spin of odd half-integral values, the matrix of order \( 2I + 1 \) may be broken up into two submatrices of order \( I + 1/2 \). When diagonalized, each sub-matrix leads to the same set of eigenvalues, due to the symmetry of the Hamiltonian for \( \pm m \) states.

In the general case, we have both magnetic and quadrupole interactions. It is convenient to define a ratio \( R \) of magnetic interaction energy \( \mu H_0 \), to quadrupole interaction energy \( \frac{e^2 qQ}{4} \).
We can discuss three general regions: $R \gg 1$, $R \ll 1$, and $R \approx 1$.

A well explored region in nuclear spin resonance experiments is that where $R \gg 1$. The eigenvalue energies in this case can be found by time independent perturbation theory and several authors have treated different aspects of this problem. In particular, a calculation was made by Volkoff (13) using perturbation theory up to third order. This showed how one might find the quadrupole interaction energy of a nucleus in a crystal, as well as the electric field gradient asymmetry parameter at the site of the nucleus, and the spin of the nucleus itself, by rotating the crystal about two arbitrary axes and measuring the variation of resonant frequencies with angular position. The theory was applied by Petch, Cranna and Volkoff (13) to an experiment on the crystal Spodumene ($\text{LiAl(SiO}_3\text{)}_2$). They obtained complete information on the quadrupole coupling of aluminum in the crystal as well as the orientation of the field gradient and its asymmetry at the site of the nucleus. Perturbation theory may also be used for the case where $R \ll 1$. This has been treated by Kruger (14), Bersohn (15), Cohen (16), and is discussed in a forthcoming review by Das and Hahn (17).

A calculation and experiment was also carried out in this laboratory by Haering (18) for the case of $\text{B}^{11}$ nuclei in kernite. A pure quadrupole line predicted from high field measurements by Waterman (19) was found, and perturbation theory was used to calculate the Zeeman splitting for $R \ll 1$. Measurements were made of the Zeeman splitting of the line up to $R = 0.2$. 

\[ R = \frac{4 \mu H_0}{e^2 q Q} \]
For the region where \( R \) is of the order of unity, no perturbation calculation will work. The Hamiltonian must be diagonalized exactly if the energy levels are to be predicted. Various methods of diagonalizing a matrix are available but in general, matrices for spin greater than unity must be diagonalized by numerical methods. Thus, no general solution can be given for the energy levels, and the best procedure is often different for different cases. We now limit the discussion to the case of spin 5/2, which fits the experiment to be described. For spin 5/2 the quadrupole interaction Hamiltonian has the following form:

\[
\mathbf{H}_Q = 
\begin{pmatrix}
W & O & S & O & O & O \\
O & T & O & V & O & O \\
S & O & U & O & V & O \\
O & V & O & U & O & S \\
O & O & V & O & T & O \\
O & O & O & S & O & W
\end{pmatrix}
\]

\[
W = \frac{A}{4} \quad T = \frac{-A}{20} \quad U = \frac{-A}{5}
\]

\[
S = \frac{A \eta}{4 \sqrt{10}} \quad V = \frac{3A \eta}{20 \sqrt{2}} \quad \eta = e^2qQ
\]

This matrix may be separated into two 3x3 sub-matrices, each of which yields the same third order secular equation for the energy levels;

\[
E^3 - 7E (3 + \eta^2) + 20 (1 - \eta^2) = 0
\]

Where the units of \( E \) are \( e^2qQ/20 \), this agrees with the equation given by Cohen (16). This cubic equation can be solved for any particular
value of $\mathcal{H}$, and then use of the quadrupole interaction constant $e^{-2qQ}$ leads directly to the expected pure quadrupole transition frequencies.

In order to calculate the energy levels related to the experimental conditions, we consider the Zeeman Hamiltonian $\mathcal{H}_Z$ for the case that the magnetic field lies in the plane of the $xz$ principal axes of the electric field gradient tensor, making an arbitrary angle with the $z$ axis, which is chosen as the axis of quantization. Note that the $x$ and $y$ directions of the system are not equivalent because of the asymmetry of the crystalline field gradient.

$$\mathcal{H}_Z = \begin{pmatrix}
L & F & O & O & O & O \\
F & M & G & O & O & O \\
O & G & N & K & O & O \\
O & O & K & -N & G & O \\
O & O & O & G & -M & F \\
O & O & O & O & F & -L
\end{pmatrix} \cdot (-1)$$

$$L = B \cos \theta \quad M = \frac{3}{5} B \cos \theta \quad N = \frac{1}{5} B \cos \theta$$

$$F = \frac{1}{\sqrt{5}} B \sin \theta \quad G = \frac{2\sqrt{2}}{5} B \sin \theta \quad K = \frac{3}{5} B \sin \theta$$

$$B = \mu H_0$$

The total Hamiltonian $\mathcal{H}$ of the system is given by

$$\mathcal{H} = \mathcal{H}_Q + \mathcal{H}_Z$$
The energy levels of the system are found by diagonalizing the matrix form
of the Hamiltonian, which is exactly equivalent to solving the eigenvalue
problem:

$$\mathcal{H}_i = E_i \psi_i$$

This leads to a secular determinant which may be written as follows:

$$\begin{vmatrix}
    a & gh & 0 & 0 \\
    \vdots & \vdots & \vdots & \vdots \\
    g & bi & j & o \\
    \vdots & \vdots & \vdots & \vdots \\
    h & i & c & k \\
    \vdots & \vdots & \vdots & \vdots \\
    o & j & d & i \\
    \vdots & \vdots & \vdots & \vdots \\
    o & 0 & o & h \\
    \vdots & \vdots & \vdots & \vdots \\
    o & o & o & h \\
    \end{vmatrix} = 0$$

$$a = -E_i - L + W = -E_i - B \cos \theta + \frac{A}{4}$$

$$b = -E_i - M + T = -E_i - \frac{3}{5} B \cos \theta - \frac{A}{20}$$

$$c = -E_i - N + U = -E_i - \frac{1}{5} B \cos \theta - \frac{A}{5}$$

$$d = -E_i + N + U = -E_i + \frac{1}{5} B \cos \theta - \frac{A}{5}$$

$$e = -E_i + M + T = -E_i + \frac{3}{5} B \cos \theta - \frac{A}{20}$$

$$f = -E_i + L + W = -E_i + B \cos \theta + \frac{A}{4}$$

$$g = F = -\frac{B \sin \theta}{\sqrt{5}}$$

$$h = S = \frac{A \mathcal{N}}{4 \sqrt{10}}$$
Fig. 1 - Energy Levels for $\theta = 0^\circ$
Fig. 2 - Transition Frequencies for $\theta = 0$
\[ i = -G = -\frac{2\sqrt{2}}{5} \sin \theta \]
\[ j = V = \frac{3A \eta}{20\sqrt{2}} \]
\[ k = -K = -\frac{3}{5}B \sin \theta \]

These values agree with the ones calculated by Lamarche (20).

2. Solution of the Hamiltonian for \( \theta = 0 \).

First, consider the case \( \theta = 0 \). Then \( g = i = k = 0 \).

We can break up the determinant into two 3 x 3 determinants by rearranging rows and columns so that the order instead of 1, 2, 3, 4, 5, 6 is 1, 3, 5, 2, 4, 6. One thus obtains two third order equations for the energy levels, which can be solved. Lamarche has carried out the solution for spodumene over the range of values from \( R = 0 \) to \( R = 4 \) using the values for \( e^2qQ \) and \( \eta \) obtained by Petch et al (13). The energy levels for the case \( \theta = 0 \) are plotted in Fig. (1). The energies are in units of \( e^2qQ \). The energy levels fall into two classes; class L states have mixtures of spin substates \( m = 5/2, 1/2, -3/2 \), while class M states are mixtures of \( m = 3/2, -1/2, -5/2 \). Due to the selection rule \( \Delta m = \pm 1 \) only transition between levels of different classes can occur so that for this orientation a total of nine transitions are possible. These nine transitions, denoted by \( \mathcal{J}_1, \mathcal{J}_2, \ldots \mathcal{J}_9 \), are indicated by arrows in Fig. 1. The expected transition frequencies are plotted versus \( R \) in Fig. 2. The class L and class M energy levels of Fig. 1 are numbered according to decreasing energy.
Transitions between energy levels for the $\theta = 0^\circ$ orientation are indicated by a single subscript, for example $J_2$. The region for $R > 3.2$ in Fig. 1 can be described by the perturbation theory treatment applicable when $R \gg 1$ (12) and experimental results for this region have already been obtained for spodumene by Petch and Cranna (13) who studied the Zeeman lines $J_1$ to $J_5$. The intensities of $J_6$ to $J_9$ become vanishingly small for $R > 3.2$.

The three pairs of lines $J_4, J_7$; $J_2, J_6$; $J_8, J_9$; in the range $R < 0.3$ can be described by perturbation theory applicable to $R \ll 1$. Although some experimental results were available in this region for other crystals with higher values of $e^2Q/Q$ than in spodumene, none were available for spodumene.

In the intermediate region $0.3 < R < 3.2$ in which perturbation theory is not applicable, no experimental results had been reported for spodumene, or any other crystal. One of the objects of this thesis was to close this experimental gap in the radio-frequency spectroscopy of nuclei in crystals for at least one specific example, by demonstrating the gradual transition from the pure quadrupole spectrum slightly perturbed by a magnetic field ($R \ll 1$) to the Zeeman spectrum perturbed by the quadrupole interaction ($R \gg 1$).

3. Solution of the Hamiltonian for $\theta \neq 0$.

The case where $\theta \neq 0$ is considerably more complicated. Here the determinant cannot be broken down, so that one is left with a sixth order algebraic equation to solve. While in principle, numerical methods
Fig. 3 - Energy Levels for $\theta = 10^\circ$
for the solutions of such equations exist, the computation over a reasonable range of $R$ and for several angles is a task which one would not undertake if it could be avoided. Fortunately, the task can be avoided. Electronic computers have become almost commonplace aids to scientific research in the past ten years, and the work of diagonalizing a $6 \times 6$ matrix can be performed in a matter of minutes on one of them. Diagonalization of matrices using electronic computers is discussed in Appendix B.

After it became apparent that the transitions in spodumene could be observed down to below 600 kc/sec the Hamiltonian was calculated for several values of the angle $\theta$ and values of $R$ from 0 to 3.2. The matrices for the Hamiltonian were submitted to the University of Toronto computer, FERUT, and in a few weeks the diagonalized matrices were returned. Some of the matrices, diagonalized at Toronto were purposely made to duplicate some of Lamarche’s calculations. The agreement between the duplicate calculations was quite satisfactory. Calculations were made for both $\eta = 0.95$ and $\eta = 0.93$.

In March 1957, a computer ALWAC III E was installed by the University of British Columbia. At several crystal positions of special interest, matrices were prepared and diagonalized on this machine.

As an example of the behaviour of energy levels for $\theta \neq 0^\circ$, the energy levels for $\theta = 10^\circ$, $\eta = 0.93$ are shown in Fig. 3. It is particularly noticeable that the energy levels do not cross. The reason for this is that unlike the case $\theta = 0^\circ$, in which the levels may be grouped into two sets of spin substates, no such grouping is possible when $\theta \neq 0^\circ$. 
The off-diagonal elements of the Zeeman Hamiltonian lead to mixing of all the spin substates, so that every eigenstate of the Hamiltonian will be a mixture of all six possible spin states and the energy levels no longer cross one another. A total of fifteen transitions will be possible in principle for $\theta \neq 0$, since there will be a non-zero probability of transition between any two levels. A second object of this work was to detect some of these fifteen possible transitions.

The system of numbering the energy states and transitions between them is shown in Fig. 3. The energy levels are numbered in order of decreasing energy and the transition between the $i$ and $j$ level is indicated by $J_{ij}$. The double subscript always indicates a transition for the case $\theta \neq 0$.

B. Transition Probabilities and Signal Intensities

Nuclear resonance transitions are usually caused by a radio-frequency magnetic field produced by rf current in a coil. The resonance condition is often detected by absorption of energy from the coil by the nuclear spins. In such a case, the signal intensity is proportional to the transition probability, other things being constant. In the experiment to be described, an induction type spectrometer was used, in which a signal voltage is induced by the rf nuclear magnetization at right angles to the rf magnetic field which produces transitions. As will be shown, the signal voltage in an induction spectrometer will not
necessarily be simply related to the transition probability.

We will now consider some of the factors which determine the signal strength in a nuclear induction spectrometer for transitions involving mixed \( m \) states. We will always use the cartesian co-ordinate system where \( Z \) is parallel to magnetic field \( H_0 \), \( X \) is parallel to the transmitter coils and to the radio-frequency magnetic field, and \( Y \) is parallel to the receiver coil.

For transitions between pure \( m \) states (such as we find for instance when looking at a proton resonance), the same signal voltage would be produced in a coil parallel to the \( Y \) axis as in one parallel to the \( X \) axis. This follows directly from the Bloch equations (21). Thus for transitions between pure spin states, an induction spectrometer and an absorption spectrometer will give the same signal intensity.

For transitions between mixed \( m \) states the signal intensity may not be the same for the two types of spectrometer. This has been pointed out for the case of pure quadrupole resonance (22) where if no steady magnetic field is applied, no induction signal can be obtained because of the degeneracy of \( \pm m \) states for quadrupole interactions. Pure quadrupole frequencies may of course be measured with an induction spectrometer by using Zeeman modulation, and measuring the derivative of the resonance curves with respect to magnetic field. Then the signals from the transitions between plus and between minus spin states add, since the frequency of one transition increases with increasing magnetic field and the frequency of the other decreases with increasing field (23).
To calculate explicitly the variation with R of received voltage in an induction spectrometer for transitions between mixed m states, we first note that the voltage detected will be due to an oscillating component of magnetization along the Y axis. Since magnetization M is proportional to the vector sum of the spins, the expectation value of dM/dt will go linearly with the expectation value of dI/dt. It is then sufficient to calculate the expectation value of dI_y/dt. Calculations of this nature for special situations have been reported in the past by Bloom et al (24) and more recently by Feynman et al (25). Recently a calculation of expectation values of I_x and I_y for a two state system where the eigenstates are known has been carried out by Dr. Bloom. The results of this calculation can be applied to the present problem. The calculations are shown in detail in Appendix A, but will be briefly discussed here.

For a many level system, one considers only two levels, whose eigenstates are \( \psi_1 \) and \( \psi_2 \), between which a transition is to be induced. The eigenstate of the two level system is

\[
\psi = a \psi_1 + b \psi_2
\]

The difference in population between the two states is

\[
n = a^*a - b^*b
\]

The expectation value of I_y is \( \langle \psi^* | I_y | \psi \rangle \). A bit of algebra and use of the time dependent Schröedinger equation leads to differential equations for the expectation values of dI_x/dt and dI_y/dt. In order to take into
account the interactions between the nuclei and their surroundings, the relaxation times $T_1$ and $T_2$ used by Bloch are phenomenologically introduced into the differential equations. Then taking the magnetic fields as:

$$H_x = 2H_1 \cos \omega t \quad H_y = 0 \quad H_z = H_0,$$

the differential equation can be solved when $n$ is assumed to have a constant value. Where the principal axes of the electrostatic gradient coincide with the external co-ordinate axes, the solution is

$$\frac{d \langle I_y \rangle}{dt} = \frac{2T_2 (PSn H_1)}{1 + (\omega - \omega_0)^2 T_2^2} \left\{ T_2 (\omega - \omega_0) \sin \omega t - \cos \omega t \right\}$$

$$P = \langle \psi_1^* | I_x | \psi_2 \rangle \quad iS = \langle \psi_1^* | I_y | \psi_2 \rangle \quad \omega_0 = \frac{E_1 - E_2}{\hbar}$$

$E_1$ and $E_2$ are the energies of the states between which transitions are to be induced. The resemblance to the Bloch equations is noticeable and when $P = S$ the solutions reduce exactly to the solution obtained by Bloch.

The important aspect of this solution with regard to the present experiment is the fact that the voltage detected will vary as $SP$. This is in contrast to the case when other types of spectrometers are used where the voltage detected just depends on the transition probability.

For certain transitions in spodumene, Volkoff and Lamarche have calculated values proportional to $P^2$ which are proportional to transition probabilities for the rf magnetic field linearly polarized in the $x$ direction.
Fig. 4 - Theoretical Variation of Signal Voltage as a Function of R
and thus to the signal intensity of an absorption spectrometer for that case. These values show quite strong variation with \( R \) over the region where \( R \) is about unity (22). However, the variation of \( S \) is even more pronounced. The value of \( S \) goes through zero where \( R \) is near unity. This makes a great deal of difference to an experimenter, for consider the strong line called \( J \) in Fig. 2. The transition probability which is proportional to \( P^2 \) goes through a maximum at \( R = 0.8 \). However, \( S \) goes to zero near this point. Thus just where the transition probability is a maximum, no signal will be observed if an induction spectrometer is used. Relative values of \( SP \) have been plotted in Fig. 4 for some of the stronger transitions in spodumene when \( \theta = 0 \) and the \( x \) and \( y \) principal axes of the electrostatic field gradient tensor are parallel to the \( X, Y \) directions respectively.

C. Signal-to-Noise Ratio

At this point it seems worthwhile to consider the factors which determine whether nuclear resonance signals will be strong enough to be detected in any particular situation. It is necessary to compare the voltages from the nuclear spin transitions to the other voltages present, which are grouped together under the general heading of noise.

The nuclear signal arises from the radio-frequency oscillation of a net magnetization in the sample. For pure magnetic resonance, the Bloch equations (21) for radio-frequency susceptibility allow us to calculate the signal voltage which can be produced.
The rf susceptibility depends on the number of nuclei present, their magnetic moments, the interactions which maintain the thermal equilibrium with the surroundings, and the intensity of the radio-frequency magnetic field which causes radio-frequency variation in the net magnetization.

An important relation which may be derived from the Bloch equations gives the value of the optimum rf magnetic field $2H_1 \cos \omega t$ in terms of the longitudinal and transverse relaxation times $T_1$ and $T_2$, and the nuclear magnetogyric ratio $\gamma$. The relation for maximum nuclear signal is

$$\gamma^2 H_1^2 T_1 T_2 = 1$$

Noise voltages arise from several sources. The Nyquist noise is present in any system. For a resistive impedance $R$ and a bandwidth for detected signals of $B$, the noise voltage $V$ is given by

$$V^2 = 4kTRB$$

$k$ is Boltzmann's constant

$T$ is absolute temperature in degrees Kelvin.

Often, larger noise voltages arise from other sources. Amplifiers invariably contribute some noise, and generally the oscillator which provides the rf magnetic field also produces noise. Electrical machinery and fluorescent lights cause fluctuations, not all of which can be eliminated from the output of the system.

It is clear however, that a calculation of signal-to-noise ratio based on only thermal noise gives us the best possible ratio. If this calculation gives a low ratio, the experiment must be redesigned or abandoned. Andrew (27) has derived a relation for the signal-to-noise voltage ratio based
on Nyquist noise and the best possible nuclear resonance signal voltage which may be calculated from the Bloch equations. Andrew's result for the ratio of signal voltage to noise voltage is

$$\frac{V_s}{V_n} = K \left( \frac{\pi N (1 + 1) h^2}{48 kT} \right) \left( V_C Q f_0 \frac{3T_2}{kT T_1} \right)^{1/2}$$

$f_0$ - resonant frequency

$V_C$ - volume of sample coil

$Q$ - quality factor of the coil

$N$ - number of interacting nuclei

$K$ - includes filling factor of sample coil and efficiency of the detection apparatus. It is never better than about 0.5

$T_2$ - transverse relaxation $\Rightarrow \frac{1}{\gamma (\Delta H)}$

$\Delta H$ - line width

$T_1$ - spin-lattice relaxation time

In the case of aluminum nuclei, for instance, a line width of 5 gauss gives $T_2 = 3 \times 10^{-5}$ seconds. $T_1$ must be calculated as well, but if for an aluminum resonance of 5 gauss in width, saturation does not occur for $H_1$ as large, say, as 0.3 gauss, then $T_1$ is shorter than 0.01 seconds.

With these estimates for $T_1$ and $T_2$ and taking

$N = 3 \times 10^{22}, Q = 50, V_C = 5 \text{ cc, } f_0 = 500 \text{ kc.}$

and using the nuclear constants of aluminum, we get 30 for the best possible signal-to-noise voltage with a bandwidth of 1 cycle per second. The constants were chosen to fit the case of a 10 gram sample of spodumene, although the
calculation does not strictly apply in this case, since the energy of the interaction in spodumene does not arise only from magnetic effects.

We certainly must divide by three since only two out of six levels enter into any one transition. This is just an order of magnitude calculation presented to show that it is not unreasonable to expect to see some of the resonances predicted by Lamarche and Volkoff for spodumene at low magnetic field.

D. **Choice of Crystal for the Experiment**

If the experiment was to be done at all, it was necessary to use a single crystal of some material, since the quadrupole effect, when mixed with magnetic interaction depends on the angle made by the magnetic field with the principal axes of the crystalline electrostatic field gradient tensor. Several types of crystals were immediately available, but all had serious drawbacks. Spodumene, for example, on which the most work had been done, has pure quadrupole frequencies below one megacycle, and early attempts to observe them had failed. Kernite, with a pure quadrupole frequency which is a bit above a megacycle and has been observed with good signal to noise ratio (18), has four different nuclear sites in each unit cell, each giving rise to a different resonance frequency for $B^{11}$, to say nothing of possible resonances from $B^{10}$ and $Na^{23}$ as well as from the protons contained in the crystal. Euclase, with pure quadrupole frequencies above a megacycle, also has two non-equivalent positions for nuclei in the unit cell (28) and attempts by Haering to detect the predicted
pure quadrupole frequency met with failure. Other crystals, on which measurements have been reported in the literature, appeared to suffer from one or more of the same drawbacks.

From these considerations, several possible procedures present themselves. A search could be made for some crystal with an asymmetric field gradient and quadrupole interaction energy of about 10 Mc./Sec., preferably a crystal in which all the nuclear sites for the nucleus in question are equivalent. A search through the literature might turn up something useful, or measurements on untried crystals might be carried out at high fields, in hopes of finding a suitable quadrupole coupling constant. The latter procedure would involve a large amount of preliminary work before the main experiment could be tried. Another more appealing solution would be to try to measure the resonance for Euclase or Kernite, since the frequencies involved for them are not too low, and high field data is readily available. However, the existence of more than one nuclear site for the nuclei in question would lead to many lines at intermediate magnetic fields, and untangling them might be a difficult problem.

Except for the rather low frequency of the pure quadrupole resonance, spodumene appeared to be an ideal crystal. It has only one nuclear site for each of Al$^{27}$ and Li$^{7}$, and aluminum has only one isotope. Thus lines from other nuclei than that being studied should not interfere. Complete experimental data for high magnetic field had been taken and several good clear crystals of fairly large volume were available. Furthermore, the intermediate field region calculations had already been
done for spodumene and the predicted resonant frequencies and relative intensities showed an interesting behaviour. Finally, it seemed worthwhile to try and demonstrate that nuclear resonance measurements could be carried out at frequencies below a megacycle, even for the relatively broad lines found in crystals. Spodumene was chosen as the most suitable crystal for the experiment.
A. Description of Samples

Spodumene is a silicate of lithium and aluminum. Its structure has been described elsewhere (29). The crystal has two good cleavage planes which intersect at an angle of 94°. Because of the symmetry of the crystal structure, the bisector of the 94° angle is parallel to one of the principal axes of the electrostatic field gradient tensor at both the aluminum and lithium sites. This turns out to be the x principal axis for aluminum.

The c axis of the crystal is parallel to the line of intersection of the two cleavage planes. Measurements at high magnetic field (13) have shown that the z principal axis of the electric field gradient tensor at the aluminum site makes an angle of 34° with the c axis. Only two of the three axes of the crystal can be easily identified visually so that the orientation of the z principal axis can be only located to within two possible positions by a simple examination of the crystal. In order to find the third axis, part of a single rotation of the crystal at high field about the x principal axis was made.

The identification of the third axis of any of the samples used was then made by comparison with the results at high field which had already been published (13).

Three different samples were used in all. The first was cut from a perfectly clear piece of spodumene so that it could be rotated about the y principal axis in the 5/8" hole of the receiver coil. The second was cut for
rotation about the x axis. It also was perfectly clear. The final crystal used was cut to fit into a $\frac{3}{4}$" hole with either the x or y axis along the receiver coil. The first two crystals had a volume of about 1 cc. and the second had a volume of about 3 cc. The larger crystal had a slightly greenish coloration and possibly contained some ferromagnetic impurity, as this crystal caused very bad pickup of the magnetic modulation in the pure quadrupole spectrometer, at low magnetic fields. Whatever impurity was present did not measurably affect the frequency of the resonance lines however, as some of them could be compared in all three crystals.

Using sealing wax, the crystals were mounted on a lucite rod and then aligned in the magnetic field. The alignment in the magnetic field could be checked at 600 kc. by looking at the splitting of the lithium line. Finally the crystal could be aligned to within one half of one degree by examination of a double line which appears at about 800 kc. at the field where the transition $\frac{1}{2}$ to $\frac{3}{2}$ is predicted.

The choice of sample has a great deal to do with the success of an experiment to measure quadrupole interactions. Impurities or imperfections in a crystal may cause broadening of the resonance lines to such an extent that they are unobservable. Measurements made at high field in various spodumene samples by Petch et al (13), showed that in some crystals, the satellite lines were weak or unobservable, while in other crystals the same resonance lines were quite strong. Even using results from a good clear crystal, the outer satellite lines, which are most dependent
on quadrupole interaction, are considerably wider than the central line which is only slightly perturbed by quadrupole interactions. This is clearly indicated by the record shown in Fig. 2 of reference (13) where the line width of the outer satellite appears to be about 15 kc.

B. Choice of Spectrometer

Considerable difficulty was anticipated in observing the spodumene transitions in the region below one megacycle. Several factors in the experiment tend to reduce the intensities of signals. Firstly, the population difference between the energy levels is directly proportional to resonant frequency, so that in going from 7 to 0.7 megacycles per second the number of nuclei which can give a useful signal is reduced by a factor of ten. Secondly, the lines in solids may be quite wide and this further reduces the maximum intensity of the lines. Not only are the lines broad, but due to the mixed quadrupole and magnetic splitting, instead of observing transitions between all the energy levels at a single frequency, we only observe them between pairs of levels. For a nucleus of spin 5/2, this means that only 1/3 of the nuclei interact with the exciting radiation of any one frequency to produce a signal.

The disadvantages of broad lines are partially compensated by the short relaxation times caused by the quadrupole interactions. This means that relatively high radio-frequency fields can be used to excite transitions. It might also be suggested that use of liquid air or even liquid
helium temperatures would increase the signal intensity by increasing the population difference between states. Unfortunately, the quadrupole interaction is somewhat temperature dependent, (30) and so the high field measurements would have to be done at the same temperature to get a consistent picture. Also, at low temperatures, the relaxation time is liable to be increased, so that the possibility of using high radio-frequency power levels would be lost, thus defeating the purpose of the low temperatures.

One method of making use of high radio-frequency power is by means of a superregenerative spectrometer (31) (32). This makes use of an oscillator which is periodically turned off, usually by pulses from a low frequency generator. During the periods of oscillation, the oscillator coil subjects a sample to an intense pulse of a radio-frequency magnetic field. The oscillator is then shut off or "quenched" for a fixed period during which oscillations in the tuned circuit die away. When the quench pulse is removed, the precessing nuclei in the sample may induce sufficient voltage in the oscillator coil to influence the restarting of the oscillator. This will happen if the oscillator frequency corresponds to a resonance frequency for nuclear transitions. Using a spectrometer of this type, Cranna was able to detect aluminum resonances in spodumene down to at least 1200 kc. and found the pure quadrupole line in kernite at about 1280 kc. (31). He felt that better signal to noise ratios could be achieved with more experience. Unfortunately, it is difficult to get a pure dispersion or absorption signal with this type of spectrometer, and also the quench frequency produces
sidebands on the central frequency so that frequency measurements of resonances are difficult.

High radio-frequency power has also been used with steady state methods. The chief difficulty here is with the added noise introduced by the oscillator. Bridge methods are often used to balance out most of the oscillator voltage. However, most bridges must be balanced at each frequency and are inconvenient where measurements are to be made over a wide range of frequency. Some experimental attempts to use bridges are reported in Appendix C.

A very satisfactory method of avoiding the oscillator noise while obtaining high rf power is provided by the induction spectrometer first developed by Bloch and co-workers. Using this spectrometer, only a small fraction of the total oscillator voltage is detected by the receiver coil, while for transitions between pure m states, the nuclear signal detected is as strong as for an ordinary absorption type spectrometer. The problem of sensitivity for mixed transitions has been discussed earlier. Using a spectrometer of this type, Haering was able to detect the kernite pure quadrupole resonance with very good signal-to-noise ratio (18). This type of spectrometer is also currently used in the commercial nuclear magnetic resonance spectrometers produced by Varian Associates.
C. The Nuclear Induction Spectrometer

1. General Design

The general design of the spectrometer used for the experiment is similar to that described by Weaver (33). Two identical transmitter coils of \( \frac{3}{4}'' \) diameter are mounted co-axially in a rigid brass box. A similar coil is wound on a hollow lucite spool and placed between the two transmitter coils and at right angles to them. A hole in the brass box permits samples to be inserted into the "receiver" coil where they may be subjected to a radio-frequency magnetic field from the transmitter coils. One transmitter coil is mounted on runners and may be moved back and forth by a screw, so as to reduce the coupling between the transmitter and receiver.

Some out-of-phase voltage is induced in the receiver coil, chiefly by eddy currents in the brass box. To control this, a small inductance loop similar to that described by Weaver was used. This consists of two turns of wire wound co-axially on a lucite rod \( 3/8'' \) in diameter. One more turn is placed in series across the end of the rod, to form a loop with axis at right angles to the axis of the rod. A 22 ohm resistor is placed in series with the inductance loops, so that the impedance of the whole is almost purely resistive. The lucite rod is inserted into a hole drilled co-axially into one of the transmitter coils. The lucite rod may be rotated without affecting the coupling of the loops to the transmitter coil but the coupling to the receiver coil may be adjusted over a continuous range of values. It is very important that the lucite rod fit snugly, otherwise it becomes almost impossible to get either a pure absorption or pure dispersion.
INDUCTION SPECTROMETER

Transmitter coils

Receiver coil

Shield

25 pf

500 K

400 pf

1000 pf

220 K

25 pf

2.5 mH

5692

400 pf

400 pf

400 pf

+300 volts

Fig. 5 - Circuit Diagram for Induction Spectrometer

Facing page 30
signal. In practice, the lucite rod was made to fit quite snugly in its hole, after a little stopcock grease had been applied to prevent binding.

The transmitter coils were made to be part of the resonant circuit of a push-pull oscillator; see Fig. 5. The capacity of the tank circuit was two gangs in series of a three gang condenser. The third part of the condenser formed a resonant circuit with the receiver coil. By making the inductance of the receiver coil and of each of the transmitter coils to be the same, both transmitter and receiver could be tuned over a range of from 500 kc/sec to 1000 kc/sec by adjusting the three gang condenser. Trimming condensers were provided for fine adjustment. The oscillator tube found to be most satisfactory was a 5692 double triode. By controlling the plate supply voltage of the oscillator tube, radio-frequency voltages of from 2 to 100 volts r.m.s. could be produced across the transmitter coils. The voltage coupled into the receiver coil from the transmitter could be reduced to below a millivolt, but in operation, a voltage of about 15 millivolts r.m.s. was induced for reasons given below. The tuned receiver coil was coupled to a three stage rf amplifier by a coupling condenser small enough to severely attenuate any audio voltages picked up by the receiver coil.

In the system used, the magnetic field was modulated at 228 cycles per second, so that nuclear resonance signals resulted in an audio-modulated radio-frequency voltage on the receiver coil. The rf amplifier had a gain of about 100, and the output was detected by a 6AL5 vacuum diode. The detected audio signal was amplified by an audio amplifier,
tuned at the modulation frequency, whose gain could be increased in steps from \(2 \times 10^3\) up to \(10^7\). The output from the audio amplifier was fed to a phase-sensitive detector of the type described by Schuster (34), and the resulting derivative of the resonance was recorded on an Esterline Angus chart recorder. The time constant on the phase sensitive detector could be varied from 2 to 200 seconds.

The first spectrometer built was 1" wide and 5" square, so as to fit between the poles of the electromagnet. At first the sides of the box were made of 1/16" brass, but this was found to be very unsatisfactory. In order to get a good nuclear spin resonance signal from the solid sample, an audio-frequency magnetic field modulation of up to 15 gauss was superimposed on the d-c magnetic field. A sheet of brass, when introduced into the combined audio-frequency and d-c field, vibrated strongly enough to be detected by touching one's finger to it. Such vibration leads to modulation of the voltage picked up by the receiver coil, and audio-frequency modulation far greater than any due to nuclear resonance is produced. Almost all of the vibration was eliminated by using sides made of 1/16" lucite, to which a sheet of 2 or 3 mil brass shimstock had been cemented.

The spectrometer is built in as symmetrical a manner as possible, in order that fluctuations in the level of oscillation and other instabilities should have a minimum effect on the receiver coil. The two sides of the transmitter coils are identical, and the centre of the tank capacitance is grounded. With the receiver coil centred between the two
transmitter coils, electrostatic coupling to the receiver should be almost completely eliminated. A Faraday shield around the receiver coil should give additional shielding from electrostatic coupling, but in practice, no notable improvement resulted from such a shield when the transmitter coils were properly balanced. Rough measurements of the noise voltage with the d-c magnetic field held constant gave an overall noise figure for the system of less than 2, indicating that very little noise is picked up from the oscillator.

The induction type spectrometer can produce either dispersion or absorption signals, depending on whether one detects the component of magnetization which is out of phase or in phase respectively with the exciting rf magnetic field. In order to get a pure signal mode, an "autodyne" signal voltage, which is either in phase or in quadrature is induced into the receiver coil. The autodyne signal is much larger than any nuclear signal. Only the nuclear signal which is in phase with the autodyne signal will be detected as amplitude modulation. It turns out in practice that the in-phase autodyne signal voltage is very easily affected by vibration, while the out-of-phase autodyne signal is almost unaffected. For this reason one generally chooses to observe dispersion signals with the induction spectrometer. The desired level of quadrature voltage was induced by means of the inductance coupling loop described above.
2. **Pure Quadrupole Induction Spectrometer**

In order to measure pure quadrupole resonances in an induction spectrometer one must sweep the frequency across the resonance, and also have a perturbing magnetic field, since at zero magnetic field, the symmetry of the quadrupole coupling leads to plus and minus m states falling at the same energy, so that the induction signals cancel.

Unfortunately, the phase of the autodyne signal induced in the receiver for any given adjustment is somewhat dependent on frequency. The chief cause of this frequency dependence seems to be that the eddy currents in the shielding depend somewhat on frequency. Thus it can be quite difficult to keep the spectrometer adjusted to observe a pure absorption or dispersion mode over a wide range of frequency.

For the experiments at several hundred gauss, space is at a premium so that the shielding must be quite close to the rf coils. However, for weak fields, the spectrometer may have almost any size, since small magnetic fields can easily be produced over a large volume. This reasoning led to the construction of an induction type spectrometer similar to the one previously described except that the shielding was at least one inch from the rf coils. The frequency of this instrument could be swept through 20% of the total value without serious change in the phase of the autodyne signal.

Using field modulation at 228 cycles per second of about 6 gauss, the pure quadrupole lines were observed in all three spodumene samples with this spectrometer. Radio-frequency magnetic fields of about
0.1 gauss peak-to-peak from the transmitter and time constants of up to
80 seconds on the phase sensitive detector were used.

3. The Magnet

For convenience in magnetic field control, measurements
of weak resonance signals are often made by setting the magnetic field
at a predetermined level and sweeping the radio-frequency across the
resonance region. This has been the customary procedure in our nuclear
resonance laboratory in the past.

When using the induction spectrometer, the phase of the
autodyne signal picked up in the receiver coil is dependent on frequency.
Thus the autodyne signal may at times contain a little bit of in-phase
component, which as stated earlier, is susceptible to vibration.
This means that if any vibration at the modulation frequency is present,
one gets drifting of the output to the chart recorder as the amount of
in-phase component of the autodyne signal changes. Even with the small
amount of vibration still present in the spectrometer after all improvements
had been made, the drift could be bad enough to cause the recorder to go
completely off scale over a sweep of 100 kc. In addition, the mixture of
modes caused by the variation in-phase of the autodyne signal as the
frequency is varied causes the shape of the resonance to become uncertain,
so that to pick a weak line out of the noise becomes very difficult.
It was therefore decided that instead of changing the frequency while
holding the magnetic field strength constant, the magnetic field would
be varied while holding the radio-frequency constant.
In order to avoid the use of d-c amplification, the magnetic field would be modulated as before. It was relatively easy to vary the field slowly over a wide range, since the current through the electromagnet already in use was controlled by a servo-system which amplifies an error signal, thereby controlling the grids of a bank of 6AS7 triodes which supply the magnet current. To get a magnetic field sweep which was linear in time, it was only necessary to add a linearly varying voltage to the error signal.

Owing to the hysteresis of the iron in the magnet, it is impossible to predict the magnetic field accurately from a knowledge of the current in the coils. The field is normally held steady by a proton resonance field control system (35); one could vary the field by slowly changing the frequency of the proton spectrometer. However, this procedure could become more and more difficult as lower fields were needed, since the proton resonance would finally become too weak to control the field, due to the low resonance frequency.

In order to have a field calibration for each run, a small probe was mounted in the brass box containing the nuclear induction system. The probe was as near as possible to the sample and contained the coil from an oscillating detector of the type designed by Collins (35). The coil was immersed in mineral oil, and provided a proton signal for frequencies 0.8 to 3 megacycles per second with a large signal-to-noise ratio. The output from the oscillating detector was attenuated and led into the same audio amplifier which amplified the detected signals from
the nuclear induction apparatus. Thus by choosing a suitable frequency for the oscillating detector, a calibration resonance line could be put on the chart at any desired field as the field swept slowly through the proton resonance. In practice, the variation of field with current was found to be linear enough to that interpolation over 20 or 30 gauss was accurate to about 1 gauss. The difference of field between the position of the proton probe and the sample coil of the nuclear induction head was measured using a sample of lithium acetate in water. A difference of from 1/2 to 3/4 gauss was found between the two positions. Since measurements were only made to an accuracy of about one gauss, because of line widths, a correction could easily be applied. A slightly more satisfactory calibration point was provided by the resonance in the copper wire of the receiver coils. Also, the Li\textsuperscript{7} in the spodumene crystal gives a resonance which may be used for field calibration.

Using the iron electromagnet which has been described earlier (35), measurements of aluminum resonances in spodumene were made down to about 600 kc and it was apparent that sufficiently good signals could be obtained to measure some of the spodumene transitions where R is of the order of unity.

In order to simplify the measurements of magnetic field, an air core electromagnet was constructed, free from ferromagnetic materials. The magnet was designed to approximate to a Helmholtz coil and consisted of two large coils, each with about 3000 turns of number 18 wire. The inner
Fig. 6 - Block Diagram of Experimental Apparatus

Facing page 57
Diameter of each coil is about 6" and the outer diameter 10". Each coil had a width of 3½". The coil forms used were made of a brass cylinder, and aluminum sheets of 3/8" thickness. Three layers of copper tubing were placed in each coil, and water could be passed through the tubing at the rate of 2 litres per minute. The magnet temperature remained quite constant at 5° to 10° below room temperature.

The current for the magnet was controlled by the same servo-system which was used to control current in the iron electromagnet. Switches were put in the system so that one could switch from one magnet to the other. For a useful gap between the coils of 2", and using 300 volts d-c from the main d-c generators of the Physics Building, it was possible to get magnetic fields up to 480 gauss. The homogeneity of the field was estimated to be about 1/2 gauss at 200 gauss over a volume of 5 cc. from the line width of a proton signal in water. This at first appears to be quite inhomogeneous, but the widths of the lines to be measured are all greater than 5 gauss, so that the field homogeneity is quite satisfactory.

Fig. 6 is a block diagram showing the experimental apparatus.

D. **Difficulties**

At the highest levels of sensitivity used, some difficulty was experienced with instability of the apparatus. The instability became larger as rf power was increased and was the chief limitation on the sensitivity
of the apparatus. It was only observed while the magnetic field was being varied and at times effects were produced which could have been mistaken for weak resonance signals. That the signals did not arise from nuclear spin resonance was evident from the fact that they were independent of the radio-frequency used in the spectrometer. The output from the spectrometer also showed a tendency to drift steadily as the field was swept over a wide range.

During a brief visit to this laboratory, Dr. Packard of Varian Associates mentioned similar difficulties which had been experienced by other workers. He felt that most of these troubles could be traced to vibrational effects of one kind or another, particularly with the type of spectrometer where metal sides are fastened to the box containing the receiver and transmitter coils. The amount and phase of the rf voltage picked up by the receiver coil is extremely dependent on the contact resistances between the sides of the box and the main part. Any vibration tends to change these resistances and thus could produce spurious signal voltages. Experimentally, the author has often noticed that although the sides of the box are fastened down with about 40 screws, the removal of one screw can have quite a pronounced effect on the rf voltage picked up by the receiver coil. This effect is much less noticeable when lucite sheets with a thin brass covering on the outer surface are used for the sides instead of 1/16" sheets of brass.
In order to eliminate possible changes in contact resistances between the walls of the box, a new spectrometer similar in principle to the earlier spectrometer was built from a single block of aluminum. Holes were bored for the receiver and transmitter coils, leaving a 1/8" clearance for coils 1" in diameter. This spectrometer would take samples up to 3/4" in diameter and was used for measurements with the large greenish crystal described earlier. However, although the larger crystal gave larger resonance signals, no significant decrease in the instability was noticed with the spectrometer made from a single block of aluminum. Tests showed also that the instability was not due to the sample. It is felt that the chief advantage of a spectrometer made from a single block is that some simplification in construction is achieved.

It was possible to get sufficient signal-to-noise ratio, even with the instability, by decreasing the bandwidth of the system and using lower levels of rf power. Careful adjustment to give pure quadrature phase for the rf voltage in the receiver coil also leads to considerable decrease in instability. This of course is a strong argument for believing the difficulty is connected with some vibrational effect in the instrument. In any case, the spectrometer even with its faults gave sufficient sensitivity to detect the resonances under investigation.

One other possible explanation may be offered for the instability. Some modulation voltage is induced into the coils of the electromagnet, which can be fed back to the servo-system controlling
the d-c current to the magnet. Changes in magnet current are associated
with changes in the loop gain of the system, so that as the magnetic field
is gradually varied there may be variations of small currents in the system
which are in phase with the modulation field and with the reference voltage
to the phase-sensitive detector. This could lead to drifting of the output
level of the spectrometer. Complete elimination of these effects is not a
simple problem, and since the purpose of this research was to observe a
certain resonance spectrum, not to develop a spectrometer, no all-out
attack has been made on the problem. These difficulties are pointed out
to assure the reader that the limits of sensitivity have not been reached,
and there is reason to believe that even weaker resonances than those
studied here could be observed if the apparatus was perfected.
CHAPTER IV

EXPERIMENTAL PROCEDURE

The measurements reported in this thesis were obtained for the most part using the iron-free electromagnet where measurements of magnetic field could be obtained by a measurement of magnet current. The current through the magnet was measured by means of a potentiometer which measured the voltage developed across a 1/2 ohm manganin resistor in series with the magnet. The manganin resistor was wound on a bakelite form and carefully annealed before being put into the system. The potentiometer was fed by several number six dry cells which were placed in a closed box to prevent rapid fluctuations in their temperature. It was calibrated regularly with a standard voltage cell. The field versus the potentiometer reading was measured from 450 gauss down to 100 gauss using Li$^7$ and proton resonances from samples placed at the position normally occupied by the crystal. No deviation from linearity was found. The spectrometer could be removed and replaced in the field within a few millimeters of its former position, but the field calibration was checked before and after each set of measurements as a precautionary measure.

All frequency measurements were made using a BC 221-A frequency meter. The crystal oscillator frequency of the meter was checked against WWV at 20 megacycles. The spectrometer oscillator frequency remained stable to much better than 0.1 kc over periods of hours, provided
the voltages on the plate or the heater of the oscillator tube were held constant.

Using the new electromagnet the spectrum of $\text{Al}^{27}$ in spodumene was measured down to about 20 gauss.

Time constants between 2 and 200 seconds were used at various times. Most of the work was done with a time constant of 20 seconds, and a field sweep rate of 5 gauss per minute. Some checks with lower time constants of the $\text{Li}^{7}$ resonances showed that the fast sweep rate led to a systematic error of about 0.5 gauss in measuring position of a resonance. However, the narrowest line width found for $\text{Al}^{27}$ resonance was 5 gauss, and the precision of measurement was limited by signal to noise ratio to about 0.5 gauss. Thus it was advantageous to apply the correction rather than to reduce the time constant or use slower field sweep. Field modulation up to 15 gauss peak-to-peak has been used. As a general rule, the broader the modulation, the easier it is to detect a line, but the poorer is the precision of measurements. Thus for some of the measurements made of $\text{Al}^{27}$, modulation widths down to 1 gauss peak-to-peak were used, but higher modulation strength was used depending on how difficult a transition was to observe.

Rf field strengths up to 0.5 gauss r.m.s. could be produced, but the increase in instability for high power made 0.1 gauss r.m.s. the most practical rf field strength.

The magnet current was supplied from either a stack of accumulators which produce 110 volts d-c or two motor generators which can produce up to 300 volts d-c when in series, or a transformer and bank
of selenium rectifiers which would provide two amps at 250 volts d-c with considerable ripple. The current to the magnet was passed through a bank of 19 6AS7 double triodes. The grids of the 6AS7's were controlled by a voltage derived from a 2 ohm resistor in series with the magnet. This voltage is balanced by a bucking voltage, and the difference goes to a d-c amplifier which controls the grids of the 6AS7 triodes in such a way as to keep the error voltage very small. The bucking voltage was changed linearly in time using the voltage from four No. 6 dry cells across a 500 ohm, 15 turn helipot. This produced a linear change in the magnet current and in magnetic field. An a-c feedback loop reduced the amount of ripple on the magnet current.

To make a measurement, the oscillator was first set accurately at the desired frequency. Then the magnetic field was set at some point above the position where a resonance was expected, and a synchronous motor driving the bucking-voltage helipot gave a field sweep which was linear in time. The output from the detection system was recorded on an Esterline Angus chart recorder. The chart of the E.A. recorder is also driven by a synchronous motor. As the reading on the field calibration potentiometer passed through a given value, a calibration mark could be put on the chart record. The potentiometer setting for which a resonance occurred was found by linear interpolation between these calibration marks.

For some of the measurements, the signals were very weak, and in order to get reasonable accuracy, it was necessary to go over the
weak resonances several times and compare the signal obtained in several runs. As an example to show clearly the advantages of comparing results of several runs, two typical recordings taken with exactly the same conditions are shown in Plate I. The runs were made with \( \theta = 5^\circ \) at 830 kc. The two lines are \( \nu_{23} \) and \( \nu_{24} \) and by comparing the two records, it is clear that no other resonances are present. The signal-to-noise ratio is somewhat lower than usual in these two runs because a small field modulation was being used.
CHAPTER V

EXPERIMENTAL RESULTS

A. Resonance Frequencies

1. Interfering Resonances

The theoretically expected transitions $\nu_1$ to $\nu_9$ for $\Theta = 0$, and the 15 transitions $\nu_{ij}$ for $\Theta \neq 0$ have been discussed in Chapter II. We now describe what has been observed experimentally, and some of the difficulties involved.

One difficulty with measurements at low frequency is that for a given frequency, the magnetic resonances of many different nuclei are found within a small range of magnetic field. When one is observing broad lines, and is consequently using broad field modulation, there is liable to be interference by unwanted signals from nearby resonances. In this experiment, nuclear magnetic resonances from three different sources have given some interference. The Cu$^{63}$ line and the $\nu_3$ line cross at about 1 megacycle/sec. Thus measurements of $\nu_3$ could only be made well above and well below one megacycle/sec. The $\nu_7$ transition runs almost on top of the Li$^7$ resonance from about 700 kc and up. This is particularly unfortunate as $\nu_7$ is rather broad and weak and the Li$^7$ line is very strong. It is fortunate, of course, that the orientations of the electrostatic gradients at the aluminum and lithium sites are such that the lithium line has almost no splitting where the $z$ principal axis
Fig. 7 - Resonance Spectrum for $\theta = 0$
at the aluminum site is parallel to the magnetic field. Otherwise three interfering resonances due to Li\textsuperscript{7} would have been present.

The other interfering resonance encountered was due to protons in the spectrometer. The first spectrometer had coils wound on lucite, and the protons in the lucite gave a line much larger and broader than any of the resonances in the crystal being studied. A second spectrometer was built using all glass coil forms. Even with this one, a strong proton signal (although much smaller than in the first spectrometer) appeared. The signal was probably due to the insulation on the receiver coil wire. In any case, this spectrometer was much more sensitive to vibrational effects, so that a spectrometer with lucite coil forms was used for all measurements. The wide proton line prevents observation of $\nu_2$ in the region from $R = 0.4$ to $R = 0.6$.

2. $\text{Al}^{27}$ Resonances for $\Theta = 0$

In Fig. 7 some of the observed resonances for $\Theta = 0$ have been plotted. The lines are the theoretically predicted resonance frequencies and the circles represent experimental measurements. The dot-dashed and the dashed line show the position of the interfering proton and Li\textsuperscript{7} resonances respectively. Only the measurements taken in the region for $R$ less than 2 are shown as this is the interesting region for which no previous measurements were available.

In order to give a better picture of the progress of this thesis, the historical order will be followed in reporting the results.
Transitions were first observed in the large iron-core electromagnet with a spodumene sample placed so that the \( z \) principal axis was within about 5° of being parallel to the magnetic field. \( \nu_3 \) was first observed at about 1200 kc, and its position could be checked easily by comparison with the nearby Cu\(^{63} \) resonance from the copper wire in the spectrometer. It was also observed at around 800 kc but could not be found at lower frequencies. The resonant frequencies observed for \( \nu_3 \) were in good agreement with prediction. Next the signal from \( \nu_2 \) was observed at 1200 kc and traced down to 600 kc at which point the field in the large electromagnet could no longer be reduced linearly.

Measurements were then commenced in the air core electromagnet. By means of measurements made on the crystal at high field, the \( z \) principal axis was aligned to within 1° with \( H_0 \). \( \nu_2 \) was now traced down to 525 kc and back to about 750 kc at around 20 gauss. Weak resonances were also observed in the vicinity of \( R = 1.2 \) at the frequencies predicted for \( \nu_7 \). The \( \nu_7 \) resonances were at first scarcely larger than the noise, but by increasing the depth of field modulation fairly creditable records could be produced.

A search was now made for the other Zeeman split quadrupole lines at fields below one hundred gauss. In this region, \( \nu_2, \nu_4, \) and \( \nu_6 \) were detected down to fields of about 20 gauss, with a signal-to-noise ratio of only about 2. The use of magnetic field sweep prevented searching below 20 gauss. No clear indication of \( \nu_7 \) could be found in the low field region,
PLATE II

$\theta = 0$

$f_0 = 675 \text{ kc}$

$\theta = 0^\circ$

$f_0 = 900 \text{ kc}$

Facing page 48
as is to be expected from the curves of Fig. 4. The transitions $\nu_8$ and $\nu_9$ predicted by Lamarche and Volkoff (36) are shown by them to have a considerably lower transition probability than the transitions $\nu_1$ to $\nu_7$. As the resonances observed at low field for $\nu_2$, $\nu_4$, $\nu_6$ were at about the limit of sensitivity, only a short search was made for $\nu_8$ and $\nu_9$. As expected, there was no detectable indication of a resonance at the fields and frequencies where they would be found. $\nu_1$ was also observed at frequencies between 1.2 and 1.5 megacycles per second. $\nu_4$ was never clearly observed above 150 gauss. No search was made for $\nu_3$ at low fields, as low frequency combined with low transition possibility made such a search seem useless.

Plate II shows photographs of records obtained for a few of the resonances at $\Theta = 0$. The upper photograph shows a run at 675 kc/sec. The large resonance at right is due to Li$^7$. At left is the resonance from $\nu_2$ and in between is a smaller resonance from $\nu_7$. A time constant of 80 seconds was used with a modulation depth of the order of 10 gauss. The field has been swept from 450 gauss to 240 gauss. The lower picture shows the sort of signal-to-noise ratio which was obtained in measurements at low field. This is a run at 900 kc showing $\nu_6$ and $\nu_4$. In order to emphasize the way in which the record is interpreted, a drawing has been made below the record to show what would be observed if the system had no noise or instability. It is possible to make such a drawing with confidence by comparing the results from a number of such runs. The records shown on
\[ \Theta = 0^\circ \]
\[ f_0 = 800 \text{ kc} \]

\[ \Theta = 1^\circ \]
\[ f_0 = 800 \text{ kc} \]

\[ \Theta = 5^\circ \]
\[ f_0 = 800 \text{ kc} \]
Plate I make the procedure clear. In the record shown of $\nu_6$ and $\nu_4$, the magnetic field was swept from about 150 gauss to about 40 gauss. For all records shown, the highest magnetic fields correspond to the right hand side of the record.

3. Al$^{27}$ Resonances for $\Theta \neq 0$

In the vicinity of 800 kc and $R$ about 1.4, $\nu_2$ was observed to apparently split into 2 equally strong lines, if the crystal was rotated by a degree or so from the $0^\circ$ setting. The splitting became greater for a larger deviation from alignment, but for frequencies of about fifty kc either higher or lower one or other of the lines would disappear.

In order to understand this effect, we must refer to the energy level diagrams of Figs. 1 and 3. At $\Theta = 0^\circ$, the energy levels $L_2$ and $M_2$ cross. The transition $\nu_2$ goes from $L_1$ to $M_2$, and for $\Theta = 0$, no transition is possible from $L_1$ to $L_2$. If $\Theta \neq 0$, levels no longer cross, all six spin substates mix into each eigenstate, as has been discussed in Chapter II, and transitions are possible between any pair of levels. For only a slight deviation from $\Theta = 0$, the transitions equivalent to $\nu_2$ will still have greatest probability, but at the value of $R$ where the levels would cross, both transitions will have about the same probability. Plate III shows resonances at 800 kc for $\Theta = 0^\circ$, $1^\circ$ and $5^\circ$ in the region of $R = 1.4$. Values of $\Theta$ are accurate to about one half of one degree. The field has been swept over about 60 gauss for each record.
Fig. 8 - Resonance Spectrum for $\theta = 5^\circ$.
Fig. 9 - Resonance Spectrum for $\theta = 10^\circ, \theta = 20^\circ$  Facing page 50
Partly because of these experimental observations, the Hamiltonian was written down for other orientations than \( \theta = 0^\circ \), and solved by the Toronto University computer, FERUT. The transition frequencies calculated from these solutions agreed with the measured frequencies of the double lines for several orientations. This agreement was especially satisfying as it showed that even with the low signal to noise ratios obtained, measurements of resonance frequencies could be made with good accuracy. It was also nice to know for sure that the transition frequencies could be measured before they were predicted. Some of the results for \( \theta \neq 0 \) have been presented in graphical form in Fig. 8 and Fig. 9. For comparison, some points for \( \theta = 0 \) are also plotted.

The solid curves shown give the theoretically predicted frequencies as a function of \( R \) for the cases shown. The slight deviation between theory and prediction measurements (which in no case is greater than the width of the resonance) is discussed later.

The insert of Fig. 8 shows the detailed behaviour of the resonances around \( R = 1.4 \), with \( \theta = 0 \) and frequency near 800 kc. No position for the crystal was found where only a single line was observed for \( \nu_2 \) in this region. This will also be mentioned later.
B. **Signal Intensities**

The calculation of the variation of signal voltage with $R$ which is discussed in Chapter II and in Appendix A resulted from an apparent discrepancy between predicted and observed transition probabilities. When measurements were first made of $\sqrt{2}$ in the region around $R = 0.8$, it was noticed that the signal fell off sharply in intensity and became almost unobservable just in the region where the transition probability was calculated to be a maximum by Lamarche. This did not indicate an error in either calculations or measurements. The signal intensity is proportional to the transition probability only when using an absorption type spectrometer where the nuclear resonance signal is detected in a coil parallel to the linearly polarized radio-frequency magnetic field which causes the transitions. The signal voltage detected in an induction spectrometer is not simply related to the transition probability. In Chapter II and in Appendix A, the procedure for calculating the variation of signal voltage with $R$ is given. The expected variation of signal voltage versus $R$ is shown in Fig. 4, and we note that in the region around $R = 0.8$, the signal voltage should go to zero just where it was in fact observed to pass through a minimum. The observation of weak resonances in this region is due to the fact that the rf magnetic field at the sample position is not completely polarized in any one direction, but has components in different directions in different parts of the sample. Clarification of this point will be given in Chapter VI.
Signal intensity depends on line width, width of magnetic modulation, frequency of the transition, relaxation times and radio-frequency power. Measurements also depend on instrument stability. Thus any quantitative measurements of signal strength would be suspect unless all these factors were taken into account. However, the signal strength of $\nu_2$ is predicted to approach zero very sharply in the vicinity of $R = 0.8$ when an induction spectrometer is used, so some measurements of relative signal voltage were made in this region, holding the modulation width and radio frequency power constant. The variation of overall spectrometer sensitivity was checked over the frequency region involved by measuring the amplitude of the central Li$^7$ line at 500 kc and 600 kc. The intensity of $\nu_2$ was found to decrease roughly as predicted, and semi-quantitative agreement with the predictions shown in Fig. 4 was obtained.

Another check on the theory can be made by comparing signal strengths of the transitions $\nu_2$ and $\nu_7$. The predicted signal voltage is only one half as large for $\nu_7$ as for $\nu_2$, near $R = 1.2$. The observed $\nu_7$ signals were only about 1/3 as strong as for $\nu_2$ (see Plate II). Thus, the relative intensities are in qualitative agreement with the predictions. The extra difference can be attributed to difference in line width.

A comparison may also be made between signal strengths for $\nu_4$ and $\nu_6$. The signal-to-noise ratio obtained for $\nu_4$ and $\nu_6$ is not very good because they are quite wide. However, the records which have been obtained show that $\nu_6$ tends to give a bigger signal than $\nu_4.$
which is in qualitative agreement with the predictions shown in Fig. 4. (See Plate II for an example of $\nu_4$ and $\nu_6$ resonances.)

C. Pure Quadrupole Measurements and Numerical Values for Quadrupole Interaction Constants

Measurements of transition frequencies versus field for $\nu_2$, $\nu_4$ and $\nu_6$ for values of $R$ below 0.4 when extrapolated to $R = 0$ indicated that the pure quadrupole frequencies were about 5 kc away from the frequencies predicted by Lamarche. For this reason a pure quadrupole induction spectrometer was built and a search was made for the pure quadrupole resonances. Unfortunately, the large spodumene sample had some impurity which caused a great deal of modulation pick-up. The pick-up was dependent on orientation which probably indicated that the impurity was localized in one portion of the crystal. In any case, only some orientations of the crystal could be used. A pure quadrupole resonance about 20 kc wide was detected at 751.5 ± 2 kc, with the $x$ principal axis parallel to the receiver coil and the $z$ principal axis parallel to the transmitter coil. The resonance was checked by putting on a d-c perturbing field of a few gauss which made the resonance split into two lines. Runs were made at several values of low magnetic field, and the Zeeman split lines converged at 751 kc. The predicted line near 789 kc was not seen clearly with this orientation.
Using another orientation, where the z principal axis made an angle of roughly 45° in the yz plane with the transmitter coil, and the x axis was still parallel to the receiver, both the pure quadrupole lines were detected. The upper one was found at 793.5 ± 2 kc. Attempts to make measurements of Zeeman splitting with the z axis parallel to a small d-c magnetic field gave no useful results as the split lines were then too weak to detect, because of the low signal-to-noise ratio. Plate IV shows two runs in which both of the pure quadrupole resonances were observed.

The disagreement with the pure quadrupole frequencies calculated by Lamarche is beyond the estimated experimental error. However, the theoretical ratio of the frequencies was calculated for values of the asymmetry parameter $\eta$ from 0.90 to 0.98 using the equation given on page 8. The ratio of 751.5 to 793.5 occurs when $\eta$ has the value 0.933. The value of $e^2qQ$ then comes out to be 2.965 megacycles per second, compared to the value of 2.960 megacycles per second used by Lamarche. The estimated probable error of 2 kc for the pure quadrupole measurements gives a probable error of .007 for $\eta$ and 10 kc for $e^2qQ$. The above values are in excellent agreement with the results of Petch et al. The slight disagreement with the Lamarche calculation arises chiefly from his use of a preliminary value for $\eta$ of 0.95, as is pointed out in the paper by Lamarche and Volkoff (36), although the final value obtained by Petch and Cranna was $0.94 \pm 0.01$. 
Values for $e^2 qQ$ and $\eta$ may also be calculated from measurements in the region where $R \approx 1$. The predicted frequency for $\mathcal{J}_2$ is almost independent of $\eta$ for $R = 0.8$, so that with only an approximate value of $\eta$, measurements of $\mathcal{J}_2$ may be used to calculate $e^2 qQ$. The value obtained from this measurement is $e^2 qQ = 2,975$ kc. which gives an average of 2,970 kc. for the two different determinations of $e^2 qQ$.

A determination of $\eta$ may also be obtained using phenomena associated with the crossing of the energy levels $L_2$ and $M_2$. The transition $\mathcal{J}_2$, between $L_1$ and $M_2$ has a high probability of being induced, while the transition $L_1$ to $L_2$ should be forbidden for $\theta = 0$. Nevertheless, just in the region of magnetic field where $L_2$ and $M_2$ cross, resonances are observed which are due to transitions between $L_1$ and $L_2$. (See insert of Fig. 8). The resonance frequency at which the two transitions are predicted to have the same frequency at the same magnetic field is dependent on $\eta$. Using the average value, $e^2 qQ = 2,970$ kc., the cross-over frequency should be 798 kc. for $\eta = 0.930$ and 794 kc. for $\eta = 0.950$. From measurements like those shown in the insert of Fig. 8, the cross-over frequency is about 797 kc. This gives us the value $\eta = 0.935$.

Although the extremely close agreement between the two determinations of $\eta$ is certainly fortuitous, the above calculation indicates that all the determinations of $e^2 qQ$ and $\eta$ are in good agreement. Table I compares the results obtained from all the different measurements of $e^2 qQ$ and $\eta$ for Al$^{27}$ in spodumene. The errors quoted for results obtained in this work are estimated probable errors based on the precision of the experimental
measurements involved.

<table>
<thead>
<tr>
<th></th>
<th>$e^2 q Q$ Me./sec.</th>
<th>$\eta$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = 0$</td>
<td>$2.965 \pm .010$</td>
<td>$0.933 \pm .007$</td>
<td>This work</td>
</tr>
<tr>
<td>$R \approx 1$</td>
<td>$2.975 \pm .015$</td>
<td>$0.935 \pm .010$</td>
<td>This work</td>
</tr>
<tr>
<td>$R \gg 1$</td>
<td>$2.950 \pm .020$</td>
<td>$0.94 \pm .01$</td>
<td>Reference (13)</td>
</tr>
</tbody>
</table>
CHAPTER VI

DISCUSSION

The main reason for undertaking the experiment was to check that the nuclear resonance spectrum for spodumene in the intermediate field region behaved according to the predictions made by Lamarche and Volkoff. The agreement with the frequency predictions indicates that the energy levels behave as predicted.

The new method for calculating signal voltage for an induction spectrometer, which has been discussed in Chapter II, gives good agreement with experimentally measured resonance voltages.

One of the interesting predictions of the calculation is that in the intermediate field region, "extra" transitions can occur which would be impossible at higher magnetic fields. One of these, the transition $\gamma 7$, between non-adjacent energy levels has been observed in the region between $R = 1.1$ and $R = 1.4$. At higher values of $R$ it is masked by the Li$^7$ resonance, and at lower values of $R$, the combination of low signal voltage and low value of $df_0/dH$ makes it impossible to detect with present techniques.

The records reproduced throughout this report show that measurements of nuclear resonance may be undertaken at frequencies below one megacycle even in the unfavourable case of broad lines and diluted samples. As an example of the sensitivity of the induction type of
PLATE V

SPODUMENE RESONANCES - 313 kc

Facing page 58
spectrometer, Plate IV shows a record taken at 313 kc/sec at $\phi = 90^\circ$
using the largest crystal of spodumene and a time constant of 10 seconds.
In this orientation, the Li$^7$ line is split in three by the quadrupole interaction.
The smaller resonance corresponds to an aluminum resonance which would
be the "central" aluminum line at high magnetic fields. Even this low
frequency is certainly not the lower limit for detection of resonances
affected by quadrupole interactions. It just happened to be a frequency
which could be easily obtained by putting an extra condenser across the
tuned circuit of the oscillator. The magnetic field has been swept from
250 to 120 gauss in the record shown.

After looking at the record of $\nu_6$ and $\nu_4$ shown in Plate II,
some readers may question the reliability of measurements made with such
a low signal-to-noise ratio. When the positions of the resonances are already
known, it might be possible to measure some spurious resonance or a bump
in the noise as a signal. This possibility was kept in mind throughout the
measurements. Since spurious signals had been found which were independent
of frequency, no measurements were accepted unless the resonance had the
expected variation in magnetic field as the frequency was shifted through
five or ten kc.

The only resonances which were so weak as to be suspect
are those for fields below 100 gauss. In order to be sure of these, it was
sometimes necessary to make two or three runs, and then only by knowing
the shape of the resonance could a good measurement be made. To an
inexperienced observer, many of the records from which measurements
were obtained look like nothing but noise. The most convincing proof that these measurements are indeed correct lies in the fact that they were used to predict a disagreement of the pure quadrupole frequencies with those predicted by Lamarche. When the quadrupole frequencies were observed in the new pure quadrupole spectrometer, the disagreement was found to be as predicted, and as mentioned earlier, further investigation of the constants involved showed that the disagreement was due only to the use by Lamarche of an inaccurate preliminary result from the high field measurements of Petch and Cranna.

The signal-to-noise ratio obtained for measurements at fields above 100 gauss is such that there can be no suggestion that any of the resonances reported are not real. Furthermore, measurements made of the transitions \( \nu_{23} \) and \( \nu_{24} \) for \( \theta \neq 0 \) were made with no prior knowledge of where these resonances should occur, and when the transition frequencies were finally calculated, agreement with experiment was obtained.

Since many of the records shown in the thesis were taken to demonstrate other points than a good signal-to-noise ratio, two selected runs are shown in Plate VI. The upper record shows \( \nu_{23} \) and \( \nu_{24} \) resonances at 800 kc for \( \theta = 5^\circ \), while the lower one shows \( \nu_2 \) and \( \nu_7 \) resonances at 660 kc for \( \theta = 0^\circ \). Time constants of 20 and 80 seconds were used for the first and second run respectively.

The curves of Fig. 4 indicate that no signal voltage should be observed in the vicinity of \( R = 0.8 \). The curves are only exactly applicable when the radio-frequency magnetic field is parallel to either one of the x or y
principal axes of the electric field gradient tensor, and the receiver coil is parallel to the other one. In the spectrometer which has been used, the radio-frequency magnetic field is produced by two transmitter coils of 1" diameter and 1/2" length. The two coils are separated by a distance of 1", so that components of magnetic field in all directions will be produced in the sample.

The component of magnetization parallel to the y principal axis of the electric field gradient tensor is the one which becomes zero around R = 0.8. Thus, if the y axis is parallel to the receiver coil axis, no signal will be detected for one particular value of R. However, if the y axis is parallel to the transmitter coil axis, non-parallel components of the rf magnetic field will still cause transitions, so that weak resonances may be detected for all values of R.

As may be seen by comparing Fig. 7 and 4, measurements were actually made close to where $\langle I_y \rangle$ goes to zero. These were obtained with the y principal axis parallel to the transmitter coils and the x principal axis parallel to the receiver coil.

Some mention must also be made about the line widths of the resonances. The line width measured is almost certainly due to quadrupole effects. The minimum width of $\gamma_2$ around 800 kc is about 5 gauss, which corresponds to a width of about 8 kc, while the width obtained for the pure quadrupole lines is about 20 kc. It is instructive to compare these widths with the width of the central aluminum line at high magnetic fields for which quadrupole interactions only appear as second order effects and the line width.
is about 5 kc or less. We also note that at high field the outer satellites for which the quadrupole interaction is more important have a width of about 15 kc. See Fig. 2 of Reference (13).

It seems clear that as the quadrupole interactions become more important, the lines become broader. This explains the low intensities obtained for the resonances below 100 gauss since in this region the important interaction is due to the quadrupole moment.

The splitting of the $\nu_2$ resonance around 800 kc as a function of magnetic field is an interesting example of the behaviour of the angular momentum wave functions. If the z principal axis of the field gradient tensor is accurately parallel to the net magnetic field, the eigenstates M2 and L2 of Fig. 1 are made up of different sets of wave functions and so they cannot interact and the energy levels can cross. If, however, the parallel condition is not satisfied, the wave functions of the two states can mix and the levels "repel" each other. Now consider the transitions $\nu_2$, $\nu_{23}$, and $\nu_{24}$. (See Figs. 1 and 3). If we go off from the $\Theta = 0^\circ$ position by say $10^\circ$, the states should be still about the same as at $\Theta = 0^\circ$, except that energy levels 3 and 4 no longer cross. The transition $\nu_2$ is similar to the transition $\nu_{23}$ at fields above the cross-over point and to the transition $\nu_{24}$ at fields below the cross-over point. Since at $\Theta = 0^\circ$, $\nu_2$ was allowed and the other transitions forbidden, then since for small deviations from $\Theta = 0^\circ$, the eigenstates will be only slightly changed, we can expect $\nu_{23}$ to be strong at high fields and $\nu_{24}$ to be
strong at low fields. At the field where the two lines would cross for a 0° setting, both lines are strong. Calculation of signal voltage by the methods of Appendix A give approximately equal values for the strength of the two lines for this region in good agreement with experimental observations.

With reference to Fig. 1 and 3, only one of the transitions corresponding to \( \nu_{23} \) or \( \nu_{24} \) should occur at any given value of \( R \), for \( \Theta = 0^\circ \). This allowed transition at \( \Theta = 0^\circ \) is denoted by \( \nu_2 \). In early work with the smaller crystals, an angular position was found where only one line was found where \( \nu_2 \) was predicted. However, in order to separate the lines from noise, a modulation of about 4 gauss peak to peak had to be used, and lines separated by 4 gauss or less would appear as one, especially with a low signal-to-noise ratio. With the larger crystal used in the final experiments, a modulation width of about one gauss peak to peak gave sufficient signal to noise. With this lower modulation, no position was found where the two lines merged into one narrow line. Even in the best position, two peaks could still be resolved, apparently separated by three to four gauss (see Plate III). The line width for a single line was 5 gauss.

No satisfactory explanation has been found for the fact that the lines do not merge. It may well be that the crystal was not properly aligned in the field although a careful search was made to find the point of merging if it existed. It is felt that the deviation from alignment was less than one half of one degree. There also appears to be a slight
discrepancy between experiment and theory for $\nu_{23}$ at $\theta = 5^\circ$. The deviation is only about one line width or less, nevertheless, it was observed consistently for two different crystals. It seems likely that the two effects are connected, but for the present, they must remain an unsolved problem.

The pure quadrupole transitions measured in spodumene appear to be the lowest in frequency which have been observed by direct methods to date. It seems that the useful range of frequencies for crystal spectroscopy extends to lower frequencies than has been generally assumed. One interesting experiment is being planned with Dr. M. Bloom to take advantage of the possibilities of low frequency measurements in crystals. Crystalline (CuCl$_2$) 2H$_2$O becomes antiferromagnetic at temperatures below 40°K. This should lead to a non-zero magnetic field at the position of protons in the crystal. The magnitude of the field is estimated to be of about the order which would give a proton resonance somewhere between 500 and 1000 kc. If the resonance can be detected with no external field, a method of measuring the variation of the internal field with temperature will be available.

Numerous pure quadrupole transitions have been predicted at frequencies well below a megacycle per second from work at high magnetic fields. Until now, scarcely any measurements of these low frequency resonances at zero magnetic field have been reported. It would be interesting to measure a large number of these low-frequency pure quadrupole resonances to see if any discrepancies arise between measurements at high and low magnetic fields, such as has been reported in reference (18) for Kemite.
Phenomenological Equations for a Two Level System

In order to determine the signal to be expected from a radio-frequency transition using an induction spectrometer, it is necessary to calculate the component of radio-frequency magnetization parallel to the receiver coil. The magnetization will be proportional to the expectation value of the appropriate spin operator.

In a many level system it is convenient to treat only those two levels between which transitions are to be observed. Then we may write the eigenfunction of the two level system as

$$\psi = a(t) \psi_1 + b(t) \psi_2$$

where $\psi_1$ and $\psi_2$ are the eigenfunctions of the steady-state Hamiltonian $H_0$ due to the time independent electric and magnetic interactions.

The total Hamiltonian of the system will be given by

$$H = H_0 + H'$$

where $H'$ represents the time-dependent interaction between the magnetic dipole moment of the nucleus and the applied rf magnetic field.

The following relations may be written

$$H_0 \psi_1 = E_1 \psi_1 \quad H_0 \psi_2 = E_2 \psi_2 \quad \omega_0 = \frac{E_1 - E_2}{\hbar}$$

The magnitude of the rf magnetic field is given by

$$H = 2H_1 \cos \omega t$$
Thus \[ \mathcal{H}' = \gamma \mathcal{H} I \mathcal{H}' = \gamma \mathcal{H} (I_x H_x + I_y H_y + I_z H_z) \]

We also define the quantities \( P, S \) and \( M \) as follows

\[
(\psi_1^* | I_x | \psi_2) = (\psi_2^* | I_x | \psi_1) = P \\
(\psi_1^* | I_y | \psi_2) = -(\psi_2^* | I_y | \psi_1) = iS \\
(\psi_1^* | I_z | \psi_2) = (\psi_2^* | I_z | \psi_1) = T
\]

\( I_x, I_y \) and \( I_z \) are the spin angular momentum operators when \( z \) is the direction of quantization. Diagonal elements of \( \mathcal{H}' \) will not be effective in producing transitions, so we may assume that all other matrix elements than the ones included in \( P, S \) and \( T \) produce negligible effects.

We write the time dependent part of the expectation value of operators \( \psi \) as \( \tilde{\psi} \). Then

\[
\tilde{I}_x = P(a^* b b^* a) \\
\tilde{I}_y = iS(a^* b - b^* a)
\]

and we note that the population difference between the two states is given by

\[ n = a^* a - b^* b \]

The time derivatives of \( a \) and \( b \) may be obtained in terms of \( P, S, T, E_1, E_2, a \) and \( b \) by use of Schrödinger's equation

\[ i \hbar \frac{\partial \psi}{\partial t} = \mathcal{H} \psi \]

since the eigenstate of the two level system must be a solution of Schrödinger's equation.
Using the above mentioned time derivatives of \(a\) and \(b\), we obtain expressions for the time derivatives of \(I_x\), \(I_y\), and \(n\), which reduce to the equation \(\frac{dI_y}{dt} = \gamma I X H\) for nuclei of spin \(1/2\).

\[
\begin{align*}
\frac{dI_x}{dt} &= \omega_0 I_y P/S - 2PS_n \gamma H_y - \left\{ I_x / T_2 \right\} \\
\frac{dI_y}{dt} &= -\omega_0 I_x S/P + 2n \gamma S(PH_x + TH_y) - \left\{ I_y / T_2 \right\} \\
\frac{dn}{dt} &= 2 \gamma \left[ H_y I_x S/P - (PH_x + TH_y) I_y / S \right] - \left\{ (n - n_0) / T_1 \right\}
\end{align*}
\]

The terms in curly brackets have been added phenomenologically following Bloch. The number \(n_0\) represents the population difference in the absence of the radio-frequency field.

We will consider the particular case where the rf magnetic field is parallel to the \(x\) axis.

\[
H_z = 0 \quad H_y = 0 \quad H_x = 2H_1 \cos \omega t
\]

For steady state conditions, \(n_0\) is constant in time. The experimentally observable component of magnetization will be parallel to the \(y\) axis, so we are interested in \(I_y\). Solving the equations we obtain

\[
I_y = \frac{2T_2 PS_n \gamma H_1}{1 + (\omega - \omega_0)^2 T_2^2} \left\{ T_2 (\omega - \omega_0) \sin \omega t - \cos \omega t \right\}
\]

Using the approximations

\[
\omega - \omega_0 \ll \omega_0 ; \quad \frac{1}{T_2} \ll \omega_0
\]

\[
(\omega_0^2 - \omega^2) + \frac{1}{T_2^2} \approx 2\omega_0 (\omega - \omega_0) + \frac{1}{T_2^2} \approx 2\omega_0 (\omega - \omega_0)
\]

A similar solution may be obtained using \(H_z = 0\) \(H_x = 0\) and \(H_y = 2H_1 \cos \omega t\).
Other cases lead to more complex solutions which will not be reproduced here.

For transitions between pure spin states for \( P = S \), the solution reduces to the result obtained from the Bloch equations.

**APPENDIX B**

Notes on Diagonalization of Matrices

The most efficient procedure for obtaining eigenvalues of a symmetric matrix is not to solve the sixth order secular equation, but to diagonalize the matrix directly, using the Jacobian method. The Jacobian method is an iterative procedure which diagonalizes one 2x2 sub-matrix at a time. For a symmetric matrix, this is particularly easy, for consider the matrix \( A \)

\[
A = \begin{pmatrix}
x & w \\
w & y \\
\end{pmatrix}
\]

Then \( U^*AU \) is the diagonalized matrix, where

\[
U = \begin{pmatrix}
\cos \varphi & -\sin \varphi \\
\sin \varphi & \cos \varphi \\
\end{pmatrix}; \quad U^* = \begin{pmatrix}
\cos \varphi & \sin \varphi \\
-\sin \varphi & \cos \varphi \\
\end{pmatrix}; \quad \tan 2 \varphi = \frac{2w}{x - y}
\]

To see how the method is applied to a larger matrix, suppose we wanted to do one step in the diagonalization of the matrix for \( \mathcal{H}_Z \) on page 9. We choose the largest off-diagonal element which in this case is \( K \) and call it \( w \). Then:

\[
x \text{ is } N \text{ and } y \text{ is } -N; \quad \tan 2 \varphi = \frac{2K}{2N}
\]
The process always converges, since the spur of the matrix, and the spur of the matrix squared are conserved, and each step shifts one of the off-diagonal elements into the spur. The procedure is ideal for a machine, since it may be repeated over and over again with no new instruction. The machine has only to decide which off-diagonal element is largest at each step. It must also stop when the off-diagonal elements have been reduced to a sufficiently small value.

Now computers generally have a quite limited number of operations which they can perform. The computer recently installed by the University of British Columbia, ALWAC III, can add or subtract, multiply, divide, compare numbers, look up numbers in its magnetic memory drum on being given the proper command, besides being able to type out numbers which are stored in certain parts of its memory. It can also choose between certain alternate operations depending on whether certain numbers are positive or negative. Information and commands are used by the machine in "hexadecimal" code. The machine can be made to translate from the hexadecimal code to ordinary decimal
numbers and vice versa. In order for the machine to do a useful computation, a program of the steps to be performed must be prepared. The programs for many of the standard calculations, such as the calculation of exponential and trigonometric functions are stored in the machine's memory and are available at any time.

A program for diagonalizing matrices up to order 8X8 by the Jacobian method was written by Dr. J. M. Daniels, and stored in the memory of the computer. The program consists of over one hundred eight-digit "words" in hexadecimal code. In the course of a computation, the machine does many more than one hundred steps, as the program is so written that many of the steps are repeated over and over. Once the program is correctly stored in the memory (one always checks this by solution of a simple standard matrix), the procedure for diagonalizing a matrix is extremely simple. The program is moved from the main memory storage to the working storage by simply typing out on the control typewriter the command 4412. After a space, the order of the matrix is typed in, 6 in our case. Then the 36 numbers composing the matrix are fed into the machine, and last, a number is typed in which will be the maximum allowed size of off-diagonal elements in the diagonal matrix. One then types in a space and the calculation starts. After from three to five minutes, the elements of the diagonalized matrix are typed out in order by the machine and it is ready for another calculation.

Plate VII shows the record obtained for the diagonalization of a particular matrix. The case shown is for $\theta = 5^0$, $R = 1.52$ and $\pi = 0.933$. 
<table>
<thead>
<tr>
<th></th>
<th>4412 6</th>
<th>-12855</th>
<th>7376</th>
<th>0</th>
<th>-1481</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>7376</td>
<td>-27771</td>
<td>9896</td>
<td>-2150</td>
<td>-1987</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>9896</td>
<td>17773</td>
<td>0</td>
<td>-2150</td>
<td>-1481</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1481</td>
<td>-2150</td>
<td>0</td>
<td>-27771</td>
<td>9896</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-1987</td>
<td>-2150</td>
<td>9896</td>
<td>-12829</td>
<td>7376</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-1481</td>
<td>0</td>
<td>7376</td>
<td>62855</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

-10772.
1.
-10.
-1.
...  
...  
-31965.
...  
...  
...  
-10.  
...  
19974.
1.
...  
...  
...  
-33301.
...  
-1.
...  
...  
...  
-7534.
...  
...  
...  
-1.

63631.
The block of numbers at top is the matrix which is to be diagonalized and the column below contains the elements of the diagonalized matrix as they were typed out by the machine. The actual position of each term in the column may be determined by noting that the machine types the elements of each row of the matrix in turn. It will be noted that the off-diagonal elements are no longer completely symmetric. This is merely due to round-off errors and does not indicate that anything has gone wrong.

APPENDIX C

Experiments on Bridge Type Spectrometers

After it was realized that the induction signal could disappear for transitions involving quadrupole interactions, some experiments were undertaken to try and find resonances using the absorption of energy from one arm of a radio-frequency bridge. It seems reasonable to expect that the oscillator noise should be balanced out here and most of the advantage of a crossed-coil spectrometer would be obtained without the disadvantage of low signal voltage for $\sqrt{2}$ at $R = 0.7$. Since field sweep was being used instead of frequency sweep the chief argument against bridges, that a bridge is hard to keep in balance over a range of frequency, becomes unimportant. Several different types of bridges were built and tested including those described by Soutif (37), Anderson (38) and Torrey (39), as well as some modifications that seemed to be worth trying.
In every case, the noise from the bridge was at least five times higher than would be obtained from pure Nyquist noise. The noise was lowest when bridges of a symmetrical type were used, and also quadrature phase unbalance gave better results than a slight in-phase unbalance, but when the oscillator power was increased to a power level comparable to that used in the inductium spectrometer, the signal to noise ratio obtainable was such that Li\textsuperscript{7} signals in spodumene could scarcely be detected at 700 kc. The attempt to see resonances using a bridge was finally given up as a waste of time. Probably the chief cause of the noise is that high currents in the tank circuits of the bridge lead to noise, which cannot be balanced out.
REFERENCES

1) Frisch, R. and Stern, O., Z. Phys. 85, 4 (1933)

2) Rabi, I. I., Millman, S., Kusch, P. and Zacharias, J. R., Phys. Rev. 55, 526 (1939)

3) Lasarew, B. G. and Schubnikow, L. W., Phys. Z. Sowjet, 11, 445 (1937)

4) Gorter, C. J., Physica, 3, 995 (1936)


14) Kruger, H., Z. Physik, 130, 371 (1951)

15) Bersohn, R., J. Chem. Phys. 20, 1505 (1952)


17) Das and Hahn, Nuclear Quadrupole Resonance Spectroscopy. Preprint to Dr. M. Bloom


21) Bloch, F., Phys. Rev. 70, 460, (1946)


30) Bayer, H., Z. Phys. 130, 227, (1951)


33) Weaver, H. E., Jr., Phys. Rev. 89, 923, (1953)

34) Schuster, N. A., R.S.I., 22, 254, (1951)


37) Soutif, M. Nuclear Paramagnetism, La Revue Scientifique, P. 203, (1951)
