A study of the E.P.R. spectrum of the calcium(OH)$_2$:gadolinium(3+) system

Barry James Fox

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A STUDY OF THE E.P.R. SPECTRUM OF THE
Ca(OH)2 : Gd3+ SYSTEM

by

Barry James Fox

A Thesis
Submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor

Windsor, Ontario
1972

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The system Ca(OH)$_2 :$ Gd$^{3+}$ was studied by electron paramagnetic resonance methods, to observe and measure ground state splitting in the Gd$^{3+}$ ion ($^8S_{7/2}$). Fine structure was observed and the angular variation seemed consistent with a trigonal field.

The Spin Hamiltonian

$$H = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \sum_{n,m} B_{nm} T_{nm} \cdot m = 0, 3, 6$$

was solved by an exact diagonalization process and the crystal field terms fitted using a multi-dimensional least squares method. The parameters were found to be

$$g_x = 1.990 \pm 0.005; \quad g_y = 1.991 \pm 0.005; \quad g_z = 1.989 \pm 0.006$$

In gauss

$$b_2^0 = -655.0; \quad b_4^0 = -11; \quad b_6^0 = +4$$

$$b_4^3 = +27; \quad b_6^3 = -170; \quad b_6^6 = -0.06$$

$$c_4^3 = +2; \quad c_6^3 = +124; \quad c_6^6 = -0.05$$

The fit had an R.M.S. error of 88 gauss for 63 lines.

It was postulated and is being tested at present that the $B_{22}, B_{42}$ and $B_{44}$ terms should be considered in the Hamiltonian. The intensity ratios were found to be $4 : 8 : 12 : 16 : 12 : 10 : 5$. 

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The fit including orthorhombic terms had an R.M.S. error of 91 gauss and so offered no improvement. Terms that are non-linear in magnetic field are to be considered next, followed by hyperfine and nuclear Zeeman terms.
ACKNOWLEDGMENTS

The author wishes to thank Dr. F. Holuj for first suggesting this problem and for his guidance during the work. The assistance with the computer analysis so readily given by Dr. W. E. Baylis is gratefully acknowledged. Thanks are also due to Bob Wilson for his help with the experimental work and to my wife, Marilyn, for assistance in recording of data and preparation of diagrams.
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CHAPTER I

INTRODUCTION AND PURPOSE OF EXPERIMENT

For S-state ions the resultant orbital angular momentum of the electrons is zero so that any degeneracy present in the state can only be due to spin. In such cases the ground state of the ion should not be split by the crystalline electric field. However, ground state splittings of S-state ions have been observed when the ions are placed in a crystalline environment.

The main purpose of this experiment was to observe and measure the ground state splittings produced when Gd$^{3+}$(6$S_{7/2}$) was placed in the trigonal crystalline field of Ca(OH)$_2$ using the methods of Electron Paramagnetic Resonance Spectroscopy.

Ca(OH)$_2$ was chosen as the host crystal as it has a relatively simple structure and provides a substitution site with trigonal symmetry. The trivalent gadolinium ion was chosen as it is an S-state ion from the rare-earth group, and could be successfully introduced into the Ca(OH)$_2$ crystal.

Some of the previous work on the trivalent gadolinium ion in various site symmetries has been carried out by Low$^1$ (cubic), Jones, Baker and Pope$^2$ (rhombic), Serway and Marshall$^3$ (trigonal), Buckmaster, Chatterjee and Shing$^4$ ($C_{3h}$ and $C_3$).
CHAPTER II

CRYSTAL STRUCTURE OF Ca(OH)$_2$

X-ray studies have shown$^{5-8}$ that Ca(OH)$_2$ belongs to the hexagonal system, with space group P(3,2/m,1), (CdI$_2$ type or D$_{3d}$$^3$). A projection of the structure is shown in Fig. II.1. Ca atoms lie in the invariant positions (0,0,0), with point symmetry D$_{3d}$. O and H atoms lie in the special positions $\pm (1/3, 2/3, z_o)$ and $\pm (1/3, 2/3, z_h)$, respectively, both with point symmetry 3m. Fig. II.1 shows 3 unit cells showing structure to 4th nearest neighbour and illustrating the relationship of the unit cell to the observed crystal habit. The outlined unit cell contains one molecule. The H positions were first postulated by Bernal and Megaw$^6$. They have since been confirmed by x-ray diffraction$^8$, neutron diffraction$^9$, and nuclear magnetic resonance$^{10}$.

The Ca(OH)$_2$ structure consists of two sheets of hydroxyls lying in the (0001) plane. A sheet of Ca atoms is sandwiched between them. Each Ca atom is surrounded by six OH groups forming a slightly compressed octahedron. Fig. II.2 is a three dimensional representation of a unit cell illustrating these octahedra. Neutron diffraction studies revealed that the thermal motion of hydrogen is in the (0001) plane only$^9,^{11}$. Consequently, there are no hydrogen bonds. The crystal is very soft (2 on Moh's scale) and has a perfect cleavage along (0001). Structural data is given in Table II.1.

Single crystals of Ca(OH)$_2$ were obtained by slow diffusion of NaOH and CaCl$_2$ in an aqueous solution free of CO$_2$ and O$_2$. They were doped with Gd$^{3+}$ during their growth.
Fig. II.1 Structure of Ca(OH)$_2$
projected on the (0001) plane. Some elements
of the $D_{3d}^3$ space group are shown on the unit
cell represented by the heavy outline:

- $\Delta$ 3-fold axis of rotation
- $\bullet$ inversion centre

- mirror plane
- horizontal 2-fold axis
- horizontal screw axis
Fig II.2 Three dimensional representation of unit cell of for Ca(OH)$_2$. The calcium ions appear at the corners of the unit cell, surrounded by an octahedron formed by the oxygen ions in planes above and below. The hydrogen ions (shaded) also lie in basal planes but further from the calcium ions.

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<td>Unit cell parameter $a_0$</td>
<td>3.5844 Å</td>
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<td>Unit cell parameter $c_0$</td>
<td>4.8962 Å</td>
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<td>Unit cell parameter $z_0$</td>
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<td>Structure parameter $z_h$</td>
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CHAPTER III

THEORY

A. Electron Paramagnetic Resonance

This phenomenon was first reported by Zavoyskii (1945)\textsuperscript{13} and refers to the magnetic resonance of permanent magnetic dipole moments of electrons. It is shown in its simplest form by a set of non-interacting paramagnetic ions, each possessing a single unpaired electron and a 'spin only' magnetic dipole moment of \( m_s g_s \beta \) (\( m_s = 1/2 \)) where \( \beta \) is the Bohr magneton and \( g_s = 2.00229 \). In a steady magnetic field \( H \), each dipole can orient itself parallel or antiparallel to \( H \), with energies \(-1/2 \, g_s \beta H\) and \(+1/2 \, g_s \beta H\) (Zeeman splitting). Magnetic dipole transitions can be induced between these two energy levels by applying a high frequency magnetic field polarised perpendicular to \( H \), and with frequency \( \nu \) such that the quantum of high frequency energy equals the separation between levels, i.e.

\[
\hbar \nu = g_s \beta H
\]

(III.1)

There is then resonance absorption corresponding to the dipoles being flipped from the parallel to the antiparallel state and induced emission corresponding to the reverse process.

While the system remains in thermal equilibrium the population of the lower energy parallel state will exceed that of the antiparallel state, so a net absorption of high frequency power results. Saturation of
the system and its accompanying loss of absorption can occur when the
rise in temperature caused by the absorption of energy results in an equal-
ization of the two populations.

In the more general case for a free ion with a resultant angular
momentum, \( J = L + S \) where \( L \) and \( S \) are the orbital and spin electronic
angular momentum respectively. The energy levels are then given by

\[
E = \pm mg \beta H \tag{III.2}
\]

where \( g \) is the spectroscopic splitting factor and is defined by

\[
g = 1 + \frac{J(J+1) + S(S+1) - L(L-1)}{2J(J+1)} \tag{III.3}
\]

and the Bohr magneton

\[
\beta = \frac{e\hbar}{4mc} \tag{III.4}
\]

\( M \) is the projection of the electronic angular momentum \( J \) onto the
magnetic field direction and so is the electronic magnetic quantum number.
The use of \( M \) is necessary as the dipole is no longer aligned with, but
instead precesses around, the magnetic field \( H \). The frequency of precession
is given by,

\[
\omega = g \frac{e}{2mc} H \tag{III.5}
\]

for the energies to correspond to the photon energy

\[
h\nu = g \beta H \tag{III.6}
\]

it can be seen that \( \Delta M \) can only take the values +1 or -1, so the selection
rule governing allowed transitions is:
\[ \Delta M = \pm 1 \] (III.7)

B. The Trivalent Gadolinium Ion

Gadolinium has the electronic structure

\[ \ldots 4f^7 5s^2 5p^6 5d^1 6s^2 \]

so that the trivalent gadolinium ion has a free ion ground state of \( ^8S_{7/2} \) in the \( 4f^7 \) configuration. This indicates that the orbital angular momentum is \( L=0 \). Consequently, the energy levels will be 8-fold spin degenerate, splitting into 8 levels when the degeneracy is completely removed as would be expected for spin angular momentum \( S = 7/2 \).

C. The Complete Hamiltonian

For a paramagnetic ion in a crystalline field in the absence of a magnetic field, the complete Hamiltonian operator is

\[ H = T + V_c + V_{so} + V_x + V_{ss} + V_{s} \] (III.8)

where

\[ T = \sum_k (p_k^2 / 2m) \] (III.9)

is the total kinetic energy of the kth electron with momentum \( p_k \) and mass \( m \) where the sum is taken over all electrons for the ion.

The Coulomb term \( V_c \) consists of

\[ V_c = -\sum_k \frac{ze^2}{r_k} + \sum \frac{e^2}{v_{ij}} \] (III.10)

The first term is the Coulomb attraction between the nucleus and the
electron summed over all electrons for the ion.

The $V_{so}$ term is the potential energy due to spin-orbit coupling and is written

$$V_{so} = \sum_{ij} \lambda_{ij} \mathbf{l}_i \cdot \mathbf{s}_j$$  \hspace{1cm} (III.11)

where $i$ and $j$ are summed over all electron $S$. Assuming Russell-Saunders coupling, then

$$\sum_i \mathbf{l}_i = \mathbf{L} \text{ and } \sum_j \mathbf{s}_j = \mathbf{S}$$  \hspace{1cm} (III.12)

so the term becomes

$$V_{so} = \lambda \mathbf{L} \cdot \mathbf{S}$$  \hspace{1cm} (III.13)

where $\lambda$ is the spin-orbit coupling constant.

The term $V_x$ represents the interaction between the paramagnetic ion with the crystal field potential

$$V_x = - \sum_k e_k \Psi(\mathbf{r}_k)$$  \hspace{1cm} (III.14)

The term $V_{ss}$ represents the magnetic dipole-dipole interaction between electrons and is written

$$V_{ss} = \sum_{jk} \frac{1}{3} \left[ S_j S_k - \frac{3S_j \cdot r_{jk} r_{jk} \cdot S_k}{r_{jk}^2} \right]$$  \hspace{1cm} (III.15)

where the sum is extended over all pairs of electrons.

The term $V_{sj}$ represents the magnetic interaction between unpaired electrons and the nuclear magnetic moments (the hyperfine term.)
D. The Spin Hamiltonian

The complete Hamiltonian as written in (III.8) is very difficult to work with, a simpler treatment devised by Abragam and Pryce\(^{14}\) makes use of the spin Hamiltonian of the system. The actual spin of the system is replaced by the effective spin \(S\) where \((2S+1)\) is equal to the number of electronic levels in the ground state.

The general Hamiltonian is then written as

\[
H = \beta \tilde{S} \cdot \tilde{g} \cdot H + \sum_{n,m} B_{nm} T_{nm} + \tilde{S} \cdot \tilde{A} \cdot \tilde{I} - g_{N}^{\beta} \tilde{g} \cdot \tilde{I} \cdot H \tag{III.16}
\]

where \(\tilde{g}\) and \(\tilde{A}\) are 2nd rank tensors. \(T_{nm}\) is a tensor operator equivalent and a function of the effective spin operator \(\tilde{S}\). The \(B_{nm}\) are crystal field parameters.

The first term is the electronic Zeeman term and the \(g\) tensor now incorporates an anisotropic component due to the spin-orbit coupling. Zero field splitting is represented by the crystal field term \(\sum_{n,m} B_{nm} T_{nm}\).

In the third term the \(A\) tensor describes the magnetic hyperfine interaction and also contains an anisotropic part due to dipolar coupling. The fourth term is the nuclear Zeeman term.

E. The Spin Hamiltonian for Gadolinium

As no hyperfine structure is observed for gadolinium at room temperature, the hyperfine term and the nuclear Zeeman term can be omitted so that the spin Hamiltonian for gadolinium can be written as

\[
H = \beta \tilde{S} \cdot \tilde{g} \cdot H + \sum_{n,m} B_{nm} T_{nm} \tag{III.17}
\]

the terms of which are explained separately in the following paragraphs.
(1) Zeeman Term

Considering a frame of reference that diagonalizes the g tensor, the Zeeman term can be written as

\[
H = \beta (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z)
\]

where

\[
h_+ = (g_x H_x + ig_y H_y); \quad h_- = (g_x H_x - ig_y H_y)
\]

\[
S_+ = (S_x + iS_y); \quad S_- = (S_x - iS_y)
\]

This can be written in terms of tensor operator equivalents

\[
T_{nm}, \quad \text{(See (III.26) and Table III.3)}
\]

\[
H = \beta g_z H_z T_{10} + \beta \left( \frac{h_+}{\sqrt{2}} T_{11} - \frac{h_-}{\sqrt{2}} T_{11} \right)
\]

(2) Crystal Field Term

The crystal field term represented by \( \sum_{n,m} B_{nm} T_{nm} \) is derived as follows. The Hamiltonian of the crystal field is given by

\[
H_{cr} = \sum_i V(x_i, y_i, z_i)
\]

where the crystal field potential \( V \) is a function of the position of the \( i \)th electron with the sum taken over all of the electrons in the unfilled shell. Assuming it satisfies Laplace's equation, \( V \) can be expanded in a series of spherical harmonics.
V = \sum_{i, n, m} \sum_{n, m} A_{nm} r^n Y_{nm}^{(\theta, \phi)} \quad \text{(III.21)}

Many of the terms will have zero matrix elements and need not be considered.

(a) All terms \( n > 6 \) will have zero matrix elements. For \( f \)-electron wave functions the probability density \( \psi \) can be expanded in spherical harmonics only for \( n \leq 6 \) so matrix elements \( n > 6 \) vanish.

(b) Similarly all terms for which \( n \) is odd have zero elements. The probability density \( \psi^* \psi \) is an even function while the potential is an odd function for odd \( n \).

(c) The term containing \( n = 0 \) is an additive constant that is set to zero.

Further reductions can only be made by considering site symmetry. As the gadolinium ion is assumed to substitutionally replace the calcium ion it will be in a site of \( D_{3d} \) point symmetry so that the trigonal form of the crystal field potential must be used. This can be derived by considering the symmetry of the appropriate spherical harmonics \( Y_{nm}^{(\theta, \phi)} \), determined by the lowest value of \( m \)

\[
\begin{align*}
  m &= 0 \quad \text{Axial} \\
  m &= \pm 2 \quad 2 \text{ fold symmetry} \\
  m &= \pm 3 \quad 3 \text{ fold symmetry} \\
  m &= \pm 4 \quad 4 \text{ fold symmetry} \\
  m &= \pm 6 \quad 6 \text{ fold symmetry}
\end{align*}
\]

and by setting

\[
A_{no}^n r^n Y_{no} = u_{no}^n
\]

and

\[
\left[ A_{nm} Y_{nm}^{(\theta, \phi)} + A_{n(-m)} Y_{n(-m)}^{(\theta, \phi)} \right] r^n = u_{n|m}^n
\]
then

\[ V_{\text{trig.}} = U_{20} + U_{40} + U_{60} + U_{43} + U_{63} + U_{66} \]  

(III.23)

Expressing the spherical harmonics in cartesian co-ordinates

TABLE III.1

\[
\begin{align*}
V_{20} &= 3z^2 - r^2 \\
V_{40} &= 35z^4 - 30r^2 z^2 + 3r^4 \\
V_{60} &= 231z^6 - 315r^2 z^4 + 105r^4 z^2 - 5r^6 \\
V_{43} &= (x^2 - 3y^2)xz \\
V_{63} &= (11z^2 - 3r^2)(x^2 - 3y^2)xz \\
V_{66} &= x^6 - 15x^4 y^2 + 15x^2 y^4 - y^6
\end{align*}
\]

where

\[ U_{nm} = D_{nm} V_{nm} \]  

(III.24)

\( A_{nm} \) and \( D_{nm} \) are related by the normalisation constants in Table III.2

TABLE III.2

\[
\begin{align*}
D_{20} &= \frac{1}{4} \sqrt{\frac{5}{\pi}} A_{20} \\
D_{60} &= \frac{1}{32} \sqrt{\frac{13}{\pi}} A_{60} \\
D_{40} &= \frac{3}{16} \sqrt{\frac{3}{\pi}} A_{40} \\
D_{63} &= \frac{1}{16} \sqrt{\frac{13.105}{\pi}} |A_{63}| \\
D_{43} &= \frac{3}{4} \sqrt{\frac{35}{\pi}} |A_{43}| \\
D_{66} &= \frac{1}{32} \sqrt{\frac{13.21.11}{\pi}} |A_{66}| \\
\end{align*}
\]

\( V \) can be written in the form \( f(r)P_{nm}(\theta, \phi) \) where \( P_{nm}(\theta, \phi) \) are assoc. Legendre polynomials. Once \( V_{20}, V_{40} \) and \( V_{60} \) are known all even potentials up to sixth degree can be found by symmetry.

(3) Operator Equivalents

As gadolinium is an \( S \) state ion

\[ L = 0 \quad \text{then} \quad J = S \]  

(III.25)
so that the total angular momentum will be the spin angular momentum $J = \frac{7}{2}$.

Within the manifold of states for which $J = \frac{7}{2}$ matrix elements for the potential operators may be replaced by appropriate angular momentum operators.

This is achieved by everywhere replacing $x, y$ and $z$ by $J_x, J_y, J_z$ with regard to the fact that $J_x, J_y$ and $J_z$ are non-commuting operators.

\[ e.g. \quad xy = \frac{1}{2} \alpha (J_x J_y + J_y J_x) \quad (III.26) \]

where $\alpha$ is a multiplying constant so that

\[ V_{20} = \alpha r^2 \left[ 3J_z^2 - J(J+1) \right] \quad (III.27) \]

This can be expressed as an angular momentum tensor operator $T_{20}$ which has been normalised incorporating the $\alpha r^2$ where

\[ T_{20} = \pm \sqrt{\frac{1}{6} \left( 3J_z^2 - J(J+1) \right)} \quad (III.28) \]

The angular momentum operators have been tabulated by Buckmaster et al 17. The ones of importance in this Hamiltonian are listed in Table III.3. (see next page).

In this form the crystal field can be simply written as:

\[ H_{cr} = \sum_{nm} B_{nm} T_{nm} \quad (III.29) \]

\[ n = 2, 4, 6 \]

\[ m = 0, \pm 3, \pm 6 \]

The spin-Hamiltonian can then be written:
\[ T_{20} = + \sqrt{\frac{1}{6}} \left[ \frac{3J^2}{2} - J(J+1) \right] \]
\[ T_{40} = + \frac{1}{2} \sqrt{\frac{1}{70}} \left[ 35J^4_z - 5 \left( 6J(J+1) - 5 \right) J^2_z + 
+ 3 \left( J^2(J+1)^2 - 2J(J+1) \right) \right] \]
\[ T_{6+3} = + \frac{1}{2} \sqrt{\frac{1}{2}} \left[ \frac{3}{2} \left( J^3_z + J \right) + J_z \left( J^3_z \right) \right] \]
\[ T_{60} = + \frac{1}{4} \sqrt{\frac{1}{231}} \left[ 231J^6_z - 105 \left( 3J(J+1) - 7 \right) J^4_z + 
+ 21 \left( 5J^2(J+1)^2 - 25J(J+1) + 14 \right) J^2_z 
- 5 \left( J^3(J+1)^3 - 8J^2(J+1)^2 + 12J(J+1) \right) \right] \]
\[ T_{6+3} = + \frac{1}{8} \sqrt{\frac{5}{11}} \left[ J^3 \left( J^3 + \left( 3J(J+1) + 59 \right) J_z \right) + 
+ 11J^3_z - \left( 3J(J+1) + 59 \right) J_z J^3 \right] \]
\[ T_{6+6} = \frac{1}{8} J^6 \]
\[ T_{1+1} = + \sqrt{\frac{1}{2}} J_z \]
\[ T_{10} = + J_z \]
\[ H = \beta g_z T_{10} + \frac{\hbar \hbar}{\sqrt{2}} T_{11} + B_{20} T_{20} + B_{40} T_{40} \]
\[ + B_{60} T_{60} + (B_{43} + i C_{43}) T_{43} - (B_{43} - i C_{43}) T_{4-3} \]
\[ + (B_{63} + i C_{63}) T_{63} - (B_{63} - i C_{63}) T_{6-3} \]
\[ + (B_{66} + i C_{66}) T_{66} + (B_{66} - i C_{66}) T_{6-6} \]  

(III.30)

F. Calculation of Matrix Elements

(1) The Hamiltonian

For a manifold of constant \( J \) with wave functions \( \Psi_m \) (\( \Psi_m \) is the \( z \) component of angular momentum), the elements in the secular matrix are the integrals

\[ \int \Psi_m^* \{ T_{NM} \}_{m'} \Psi_{m'} \ d\gamma = \langle m | T_{NM} | m' \rangle \]  

(III.31)

where \( T_{NM} \) transform as \( Y_N^M \) and vanish unless \( m = m' + M \),

\[ M = m - m' \]

(Proof by use of Wigner coefficients, Condon and Shortley, 1951\(^{20} \)).

Using this theorem it can be seen that as \( M \) can only take the values 0, \( \pm 1, \pm 3, \pm 6 \), which establishes the non-zero matrix elements of the \( T_{NM} \).

Using the tabulated numerical values for the matrix elements of the angular momentum Tensor Operators, the spin Hamiltonian matrix is set up as in Table III.4.
<table>
<thead>
<tr>
<th>$\pm \frac{7}{2}$</th>
<th>$\pm \frac{5}{2}$</th>
<th>$\pm \frac{3}{2}$</th>
<th>$\pm \frac{1}{2}$</th>
<th>$- \frac{3}{2}$</th>
<th>$- \frac{5}{2}$</th>
<th>$- \frac{7}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left&lt; \frac{7}{2} \right</td>
<td>$</td>
<td>$\left&lt; \frac{5}{2} \right</td>
<td>$</td>
<td>$\left&lt; \frac{3}{2} \right</td>
<td>$</td>
<td>$\left&lt; \frac{1}{2} \right</td>
</tr>
<tr>
<td>$\frac{7}{2} h_{\parallel} + \frac{7}{2} h_{\perp}$</td>
<td>$\frac{5}{2} h_{\parallel} + \frac{5}{2} h_{\perp}$</td>
<td>$\frac{3}{2} h_{\parallel} + \frac{3}{2} h_{\perp}$</td>
<td>$\frac{1}{2} h_{\parallel} + \frac{1}{2} h_{\perp}$</td>
<td>$-\frac{1}{2} h_{\parallel} - \frac{1}{2} h_{\perp}$</td>
<td>$-\frac{3}{2} h_{\parallel} - \frac{3}{2} h_{\perp}$</td>
<td>$-\frac{5}{2} h_{\parallel} - \frac{5}{2} h_{\perp}$</td>
</tr>
<tr>
<td>$+ \frac{7}{10} B_{60}$</td>
<td>$+ \frac{5}{10} B_{60}$</td>
<td>$+ \frac{3}{11} B_{60}$</td>
<td>$+ \frac{1}{11} B_{60}$</td>
<td>$- \frac{3}{11} B_{60}$</td>
<td>$- \frac{5}{11} B_{60}$</td>
<td>$- \frac{7}{11} B_{60}$</td>
</tr>
<tr>
<td>$+ \frac{7}{2} h_{-}$</td>
<td>$+ \frac{5}{2} h_{-}$</td>
<td>$+ \frac{3}{2} h_{-}$</td>
<td>$+ \frac{1}{2} h_{-}$</td>
<td>$- \frac{1}{2} h_{-}$</td>
<td>$- \frac{3}{2} h_{-}$</td>
<td>$- \frac{5}{2} h_{-}$</td>
</tr>
<tr>
<td>$- \frac{12}{11} \left( B_{43} - iC_{43} \right)$</td>
<td>$\frac{10}{11} \left( B_{43} - iC_{43} \right)$</td>
<td>$\frac{1}{2} h_{-} - \frac{5}{2} \frac{1}{2} B_{20}$</td>
<td>$+ \frac{15}{11} B_{40}$</td>
<td>$- \frac{15}{11} B_{60}$</td>
<td>$+ \frac{15}{11} B_{80}$</td>
<td>$+ \frac{15}{11} \left( B_{43} + iC_{43} \right)$</td>
</tr>
<tr>
<td>$- \frac{12}{11} \left( B_{43} - iC_{43} \right)$</td>
<td>$+ \frac{5}{11} \left( B_{43} - iC_{43} \right)$</td>
<td>$+ \frac{3}{2} h_{+}$</td>
<td>$- \frac{3}{2} h_{+}$</td>
<td>$+ \frac{3}{2} h_{+}$</td>
<td>$+ \frac{3}{2} h_{+}$</td>
<td>$+ \frac{3}{2} h_{+}$</td>
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<tr>
<td>$+ \frac{12}{11} \left( B_{43} - iC_{43} \right)$</td>
<td>$\frac{10}{11} \left( B_{43} - iC_{43} \right)$</td>
<td>$\frac{1}{2} h_{+} + \frac{5}{2} \frac{1}{2} B_{20}$</td>
<td>$+ \frac{15}{11} B_{40}$</td>
<td>$- \frac{15}{11} B_{60}$</td>
<td>$+ \frac{15}{11} B_{80}$</td>
<td>$+ \frac{15}{11} \left( B_{43} + iC_{43} \right)$</td>
</tr>
</tbody>
</table>

**TABLE III.4.**
Where the crystal field parameters are related to the conventional parameters \( b_n^m \) by:

\[
\begin{align*}
 b_2^0 &= \sqrt{\frac{3}{2}} B_{20} \\
 b_4^0 &= 3 \sqrt{\frac{10}{7}} B_{40} \\
 b_6^0 &= \frac{315}{\sqrt{231}} B_{60} \\
 b_4^3 &= 15 \sqrt{\frac{2}{3}} B_{43} \\
 b_6^3 &= \frac{315}{2} \sqrt{\frac{5}{11}} B_{63} \\
 b_6^6 &= \frac{315}{2} B_{66}
\end{align*}
\]

For computational ease the parameters are expressed in kilogauss, as \( B_{nm} \text{ (kg.)} = 0.0935 \, B_{nm} \text{ (cm}^{-1}). \)

The values of the matrix elements of the tensor operator equivalents used in the calculation of the Hamiltonian, for a manifold \( J = \frac{7}{2} \) are given in Table III.6. (see next page).

(2) The Derivative Spin Hamiltonian

In the fitting process the matrix elements of the derivative Hamiltonian (DH) are required. The matrix elements of DH are the derivatives with respect to each parameter of the corresponding elements in the matrix \( H \) taken one at a time. Each matrix will consist of only one set of elements and their complex conjugates, for example the derivative matrix with respect to the parameter \( B_{43} \) will only contain elements parallel to the diagonal but in the 3 off diagonal position and its complex conjugate on the other side of the diagonal. So the matrix elements, the parameter and the off diagonal position can be represented as in Table III.7.
<table>
<thead>
<tr>
<th>Table III.7</th>
</tr>
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<tbody>
<tr>
<td>$DH(GX) = -\frac{T_{11}}{2} H_x$</td>
</tr>
<tr>
<td>$DH(GZ) = T_{10} H_z$</td>
</tr>
<tr>
<td>$DH(B40) = T_{40}$</td>
</tr>
<tr>
<td>$DH(B43) = T_{43}$</td>
</tr>
<tr>
<td>$DH(B63) = T_{63}$</td>
</tr>
<tr>
<td>$DH(B66) = T_{66}$</td>
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TABLE III.6.

<table>
<thead>
<tr>
<th>( J )</th>
<th>( J_z )</th>
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<th>( J )</th>
<th>( J_z )</th>
<th>Matrix Element</th>
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<td>1.224745D 00</td>
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<td>5/2</td>
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<td>1/2</td>
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<td>-1.870829D 00</td>
<td>7/2</td>
<td>5/2</td>
<td>-1.870829D 00</td>
</tr>
</tbody>
</table>

\( J_z \) represents the initial state of \( T_{nm}(7/2) \) and the final state for \( T_{n-m}(7/2) \).
CHAPTER IV

INSTRUMENTATION

A. K-Band Spectrometer

The k-band spectrometer was of balanced bridge design, using a circulator, with the microwave frequency stabilized against the sample cavity. A block diagram of the system is shown in Fig. IV 1. The microwave power was supplied by a Varian model YA 98M reflex klystron producing 30 milliwatts of power.

(1) Klystron Stabilizer

The klystron frequency was stabilized to the cavity resonant frequency using a Teltronic Model KSLP Klystron Stabilizer. The stabilizer works on the principle of automatic-frequency control (A.F.C.). A sine wave modulation of approximately 70 KHz was impressed on the reflector voltage, thus causing a small amount of frequency modulation. If the klystron frequency is tuned at or near the cavity resonant frequency, the output detected by the A.F.C. detector will contain a 70 KHz component. The A.F.C. signal is amplified and then applied to the phase sensitive detector (P.S.D.), built into the stabilizer, which compares the signal with the original modulation signal. The result is a D.C. error voltage with a polarity and magnitude proportional to the difference between the klystron oscillator frequency and the resonant frequency of the cavity. The error voltage is applied to the reflector of the klystron in such a manner that the klystron frequency is pulled back to the frequency of the cavity.

20
Fig. IV.1 BLOCK DIAGRAM OF K BAND SPECTROMETER
(2) Microwave Circuit

Microwaves are prevented from re-entering the klystron by use of an isolator, which is a two-terminal pair microwave ferrite device which makes use of the Faraday effect to permit transmission of microwaves in one direction and prevents their transmission in the opposite direction. A tuneable cylindrical cavity is used as a wavemeter, and an attenuator is used to control the power reaching the sample cavity which may be necessary in cases of saturation.

A three port circulator is used to allow transmission of klystron power to the cavity and power reflected at resonance from the cavity to the detector, without power going directly to the detector or any reflected power returning to the klystron arm. The cavity arm can be matched to the klystron arm by means of a slide-screw tuner. An E.P.R. absorption in the cavity then causes a mismatch, so that power is reflected from the cavity into the detector arm. In practice the cavity is slightly mismatched in order to allow sufficient power to bias the detector crystal.

The magnetic resonant absorption signal is detected by the crystal detector. The resonant signal is pre-amplified and then fed into the Princeton Applied Research (P.A.R.) model JB-6 Lock-in Amplifier, which compares the phase and frequency of the resonant signal with the original 100 KHz modulation signal in a similar way to the P.S.D. (previously described) of the A.F.C. The result is a derivative signal proportional to the resonant signal, which can be displayed on the oscilloscope or chart recorder as a function of magnetic field. To allow display on the oscilloscope the magnetic field is modulated at 60 Hz with a 'Variac', in addition to the 100 KHz. The horizontal sweep of the oscilloscope is
connected to a 60 Hz source and synchronised with the modulation using a phase shifter. The method of oscilloscope display allows one to observe E.P.R. signals when both the magnetic field and crystal orientation are varied. As such it provides a rapid means of studying angular variation.

The cylindrical cavity used is of glass having the inside surface sputtered with gold. Operating in the TE011 mode the cavity has been successfully used in this laboratory prior to this. Incorporated with the cavity is a rotating mechanism previously developed in this laboratory. It allows rotation of the crystal about a horizontal axis which when combined with rotation of the magnet about a vertical axis means any crystal orientation can be reached for anisotropy studies.

(3) External Magnetic Field and Modulation

The external magnetic field is produced by a 12 inch Varian electromagnet with a 3.5 inch gap and rotating base. The magnet is stabilized by a Fieldial model V-FR 2503 (Varian) control unit, which keeps the field value constant to within one Gauss for several hours. It is possible to get a linear field sweep up to 20 K Gauss.

Magnetic field modulation at 100 KH z is generated by an oscillator built into the P.A.R. Lock-in amplifier. This signal is amplified externally and applied to two Helmholtz coils connected in series and mounted on either side of the cavity.

B. Proton Magnetometer

Measurements of magnetic field strength are obtained by means of a proton magnetic resonance oscillator method using an external marginal oscillator, tuning circuit and amplifier, together with a wide band amplifier.
and electronic counter, Hewlett-Packard No. 5253. Several complementary probes using rubber as a proton source have been constructed in order to cover the wide frequency range required.
CHAPTER V
EXPERIMENTAL PROCEDURE

A. X-Band

Ca(OH)$_2$ crystals doped with Gd$^{3+}$ were investigated using an X-band spectrometer. Preliminary work indicated small signals whose intensity decreased as the field moved from the crystal axes. The impossibility of obtaining a complete angular variation made it necessary to move to K-band for the increased sensitivity.

B. K-Band

(1) Crystal Orientation

The symmetry of the crystal habit together with perfect cleavage in the basal plane allowed the crystallographic axes to be determined visually within 2°. The crystal was glued with the pin parallel to c-axis [0001] as the tabular nature of the crystal caused the cavity resonance to move outside the klystron range as the crystal rotated for any other mounting.

The magnetic axes of the crystal were determined searching orientations that represented simultaneous turning points of the resonance lines for rotation of the magnet and the crystal. These orientations were plotted on a Wulff net to check that they were mutually perpendicular.

The relationship of the axis of crystal rotation to that of the magnet rotation was checked. A determination was made of the collapse point of a pair of lines on the positive side of the magnet, with the field strength constant the crystal was rotated through exactly 180° and the
collapse point of the same pair of lines searched for on the negative side of the magnet. The midpoint of the two magnet orientations was the axis of crystal rotation. As a result all readings on the magnet scale had to be corrected by \(-1.4^\circ\) before plotting on the Wulff net.

(2) Angular Variation

From the positions of the three axes the planes perpendicular to each axis but containing the other two axes were plotted. An angular variation was carried out with a \(10^\circ\) interval for the magnetic field direction moving in each of these planes in turn, \(XY(0001)\), \(XZ(1\bar{2}10)\) and \(YZ(1\bar{0}\bar{1}0)\).

(3) Measurement of Magnetic Field

In order to use the proton magnetometer for magnetic field strength measurements a new set of probes had to be constructed to extend the upper limit of measurement from 30 MHz to the 53 MHz frequency of the high field resonance line. As the coaxial cable from the oscillator to the probe formed part of the tuning circuit it was possible to increase the frequency by shortening the cable and reducing the number turns in the inductor enclosing the proton source (rubber). The frequency was increased to 60 MHz but the intensity of the proton signal became too low to work with.

A satisfactory signal intensity and frequency range was obtained by decreasing the capacitance of the cable by using a grounded brass tube as shielding with the current carried to the inductor by two stiff wires separated from each other and the shielding by spacers set at intervals along the tube, (see Fig. V.1). The change of range of X-band resonators using this probe is given in Table V.1.
TABLE V.1

<table>
<thead>
<tr>
<th>Resonator Number</th>
<th>X-Band Unit MHz</th>
<th>K-Band Unit MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>10.8 - 16.1</td>
<td>13.1 - 22.5</td>
</tr>
<tr>
<td>6</td>
<td>14.5 - 21.7</td>
<td>18.7 - 32.0</td>
</tr>
<tr>
<td>7</td>
<td>20.0 - 30.0</td>
<td>31.4 - 56.3</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>34.5 - 61.5</td>
</tr>
</tbody>
</table>

Actual measurements were made using a double beam oscilloscope. The crystal rotator and magnet scale were set at the required orientation. Each E.P.R. line in turn was centred on one of the oscilloscope beams, using the second beam the P.M.R. line was tuned to the E.P.R. line. The frequency of oscillation was then read from the digital output of the electronic counter. This frequency can be converted to magnetic field strength using the relation

\[ h\gamma = \frac{\hbar}{g_P \beta_N^H} \]

\[ H = \frac{h}{g_P \beta_N^H} \gamma \]  

\[ H(\text{K Gauss}) = 0.234869 \, \gamma(\text{MHz}) \]

where

- \( H \) is magnetic field strength
- \( h \) is Planck's constant
$g_p$ is the proton $g$ value

$\beta_N$ is the nuclear magneton

$\gamma$ is the frequency of oscillation.

The accuracy of positioning the least intense E.P.R. lines was improved by using the chart recorder. With the field value set close to resonance, the field was swept over 50 gauss tracing the line on the chart thus allowing the exact centre to be marked and the field backed up to that point using the incremental field setting. The method was checked using the DPPH marker line and there was no loss in accuracy compared to a visual method.

(4) Measurement of Microwave Frequency

A small amount of the free radical $\alpha, \alpha'$-diphenyl-$\beta$-picryl hydrazyl was included with the sample to act as a marker to measure the microwave frequency using the relation

$$h\nu = g_D \beta H_D$$

$$\gamma = \frac{g_D \beta}{h} H_D$$

(V.2)

where $\gamma$ is the microwave frequency

$g_D$ is DPPH $g$ value = 2.0036

$H_D$ is the field value of the DPPH resonance.
CHAPTER VI
DEVELOPMENT OF COMPUTER PROGRAMME

A. The Method

The computer analysis was first attempted using a method for exact diagonalization of the generalized spin-Hamiltonian based on a program obtained from Buckmaster et al. However the necessity of measurements at two frequencies for each orientation made the program unsatisfactory for use in temperature dependence studies to follow.

A method of parameter fitting using multi-dimensional Newton-Raphson Least-Squares Minimization developed by Dr. W.E. Baylis was used so that the program could be generalized. This enabled it to accept data at any orientation and to fit a curve using data from different orientations rather than different frequencies.

The one dimensional Newton-Raphson Method is obtained analytically from following condition on the Taylor's series expansion.

\[ f(x_n + h) = f(x_n) + h f'(x_n) + \frac{h^2}{2!} f''(x_n) + \ldots = 0 \quad (VI.1) \]

where \( x_n \) is an approximation of the root of the equation. This can be written in partial derivative form as:

\[ \frac{\partial}{\partial x_n} f(x_n + h) = \frac{\partial}{\partial x_n} f(x_n) + h \frac{\partial}{\partial x_n} f'(x_n) + \ldots = 0 \quad (VI.2) \]

The problem of fitting the experimental data can be overcome in the following way. The Hamiltonian can be expressed as a function of a number of fitting parameters \( p_i (i = 1, 2, \ldots I_{\text{max}}) \), the experimentally measured magnetic field values \( B_i \), and other experimental parameters necessary
such as orientation $\vec{k}$ or temperature $T$. $B$ is a function of orientation so that the resonant fields occur as $(N-1)$ values for each of $M$ orientations where $N$ will represent the degeneracy of the ground state. So the Hamiltonian can be expressed as

$$H = (p_1, p_2, \ldots p_T, B, \vec{k}, T, \ldots )$$  \hspace{1cm} (VI.3)

The Hamiltonian is represented in an $n$-dimensional basis $\{|\alpha\rangle\}$. The matrix elements for the Hamiltonian and its first and second derivatives with respect to the parameters must be known or able to be calculated

$$<\alpha|H|\beta>$$  \hspace{1cm} (VI.4)

$$<\alpha|\partial H/\partial p_i|\beta>$$  \hspace{1cm} (VI.5)

$$<\alpha|\partial^2 H/\partial p_i \partial p_j|\beta>$$  \hspace{1cm} (VI.6)

The matrix elements of (VI.4) are given in Table III.4 while those for (VI.5) are given in Table III.6. As the parameters occur linearly in the Hamiltonian with no cross products the elements of (VI.6) will be zero.

For each set of external parameters $(B, \vec{k}, T, \ldots)$ (in this case for $M(N-1)$ resonant field values), the Hamiltonian is diagonalized using the subroutine CEIGEN (see appendix). The subroutine is basically an extension of the Jacobi method to Hermitean matrices$^{23,24}$ and is double precision, complex.

A new set of basis vectors $\{|i\rangle\}$, (in terms of the original set $\{|\alpha\rangle\}, |i\rangle = \sum_\alpha \langle \alpha | i \rangle |\alpha\rangle$) is then obtained in which the Hamiltonian is diagonal

$$<i|H|j> = \delta_{ij} E_i$$  \hspace{1cm} (VI.7)
The difference between one adjacent pair of eigenenergies 
\((E_{k_1} - E_{k_2})\) will correspond to the transition energy experimentally determined from measurement of the microwave frequency \(\gamma_k\). The correspondence between the pair of eigenenergies chosen and the resonant field representing that transition must be known. In this case the correspondence was determined and the programming simplified by taking all measurements at orientations where the resonant lines were separated and in order.

A least squares sum is formed from:

\[
\left\{ (E_{k_1} - E_{k_2}) - \gamma_k \right\}^2
\]

\[
= \left\{ (E_{k_1} - E_{k_2}) - \frac{g_D H_D}{g_S} \right\}^2
\]  \hspace{1cm} (VI.9)

where the transition energy in (VI.9) is expressed in units of gauss and is determined from the resonant field of the DPPH(\(H_D\)). The value of the least squares sum \(f\) is then determined by summing over the total number of transitions measured \((N-1)M\) and dividing by the number of degrees of freedom \((N \text{ free} = \text{number of transitions} - \text{number of parameters})\).

The multi dimensional Newton-Raphson method finds the value of \(p = (p_1, p_2, \ldots, p_i)\), representing a vector in \(i\)-dimensional space where \(i\) is the number of parameters, such that \(\frac{\partial f}{\partial p_i} (p) = 0\) by solving iteratively the equation for the displacement \(\delta\) is

\[
\frac{\partial}{\partial p_i} f(p + \delta) \approx \frac{\partial}{\partial p_i} f(p) + \sum_j \frac{\partial^2}{\partial p_i \partial p_j} f(p) \delta_j = 0
\]  \hspace{1cm} (VI.10)

The solution is:

\[
\delta_i = - \sum_j M_{ij} \frac{\partial}{\partial p_j} f(p)
\]  \hspace{1cm} (VI.11)
where \( ((M_{ij}) \) is the inverse of \( \left( \frac{\partial^2}{\partial p_i \partial p_j} f(p) \right) \)

and

\[
\sum_j M_{ij} \frac{\partial^2}{\partial p_j \partial p_i} f(p) = \delta_{ii},
\]

The inversion is carried out by the subroutine DMINV (see appendix). The value of \( \delta_i \) is then added to \( p_i \) to give the new estimate of the parameter.

The first and second derivatives of the least squares sum \( f \) required in the calculation are determined using perturbation theory.

\[
\frac{\partial f}{\partial p_i} = \frac{\partial}{\partial p_i} \sum_k \left[ \left( E_{k1} - E_{k2} \right) - \frac{\varepsilon_D H_D}{\varepsilon_s} \right]^2
\]

\[
= 2 \sum_k \left( \frac{\partial E_{k1}}{\partial p_i} - \frac{\partial E_{k2}}{\partial p_i} \right) \frac{\left( E_{k1} - E_{k2} \right) - \frac{\varepsilon_D H_D}{\varepsilon_s}}{N_{\text{free}}}
\]

\[\text{(VI.12)}\]

and

\[
\frac{\partial^2 f}{\partial p_i \partial p_j} = 2 \sum_k \left\{ \left( \frac{\partial E_{k1}}{\partial p_i} - \frac{\partial E_{k2}}{\partial p_i} \right) \left( \frac{\partial E_{k1}}{\partial p_j} - \frac{\partial E_{k2}}{\partial p_j} \right) \right. \\
- \left. \left( \frac{\partial^2 E_{k1}}{\partial p_i \partial p_j} - \frac{\partial^2 E_{k2}}{\partial p_i \partial p_j} \right) \frac{\left( E_{k1} - E_{k2} \right) - \frac{\varepsilon_D H_D}{\varepsilon_s}}{N_{\text{free}}} \right\}
\]

\[\text{(VI.13)}\]

where

\[
\frac{\partial E_k}{\partial p_i} = \lim \left\{ \left( E_k(p + \delta_i \hat{v}) - E_k(p) \right) \frac{\delta_i}{\delta_i} \right\}
\]

\[\text{(VI.14)}\]

where \( \hat{v} \) is a unit vector in \( i \)-dimensional parameterspace and where.
\( E_k(p + \Delta_i \hat{\Delta}) \) is the eigenenergy (corresponding to \( E_k(p) \) of the Hamiltonian \( H(p + \Delta_i \hat{\Delta}) \) to first order in \( \Delta_i \)

\[
H(p + \Delta_i \hat{\Delta}) \approx H(p) + \frac{\partial H(p)}{\partial p_i} \Delta_i
\]  
(VI.15)

Using perturbation theory the eigenenergy can also be expressed to first order in \( \Delta_i \)

\[
E_k(p + \Delta_i \hat{\Delta}) = E_k(p) + \langle k | \frac{\partial H}{\partial p_i} | k \rangle \Delta_i
\]  
(VI.16)

and consequently

\[
\frac{\partial E_k}{\partial p_i} = \langle k | \frac{\partial H}{\partial p_i} | k \rangle
\]  
(VI.17)

Similarly

\[
\frac{\partial^2 E_k}{\partial p_i \partial p_j} = \lim_{\Delta_i, \Delta_j \to 0} \frac{E(p + \Delta_i \hat{\Delta} + \Delta_j \hat{\Delta}) - E(p + \Delta_i \hat{\Delta}) - E(p + \Delta_j \hat{\Delta}) + E(p)}{\Delta_i \Delta_j}
\]  
(VI.18)

Now to second order in \( \Delta \)'s

\[
H(p + \Delta_i \hat{\Delta} + \Delta_j \hat{\Delta}) = H(p) + \frac{\partial H}{\partial p_i} \Delta_i + \frac{\partial^2 H}{\partial p_i \partial p_j} \Delta_i \Delta_j + \frac{\partial H}{\partial p_j} \Delta_j + \frac{1}{2} \left( \frac{\partial^2 H}{\partial p_i^2} \Delta_i^2 + \frac{\partial^2 H}{\partial p_j^2} \Delta_j^2 \right) + \frac{\partial^2 H}{\partial p_i \partial p_j} \Delta_i \Delta_j
\]

\[
= H(p) + V
\]  
(VI.19)

where \( V \) may be considered a small perturbation. As the parameters appear linearly in the Hamiltonian the last term goes to zero. By second order
perturbation, the eigenenergies are shifted to

\[ E(p + \delta_1 \hat{p} + \delta_2 \hat{p}_j) = E(p) + \langle k| V| k \rangle + \sum_{\ell \neq k} \frac{\langle k| V| \ell \rangle \langle \ell| V| k \rangle}{E_k - E_\ell} \]  

(VI.20)

Thus

\[ \frac{\partial^2 E}{\partial p_i \partial p_j} = \langle k| \frac{\partial^2 H}{\partial p_i \partial p_j} | k \rangle + 2 \sum_{\ell \neq k} \frac{\langle k| \frac{\partial H}{\partial p_i} | \ell \rangle \langle \ell| \frac{\partial H}{\partial p_i} | k \rangle}{E_k - E_\ell} \]  

(VI.21)

where the matrix elements \( \langle k|M|\ell \rangle \) written in terms of the old basis are

\[ \langle k|M|\ell \rangle = \sum_{\alpha, \beta} \langle k|\alpha\rangle \langle \alpha|M|\beta\rangle \langle \beta|\ell \rangle \]  

(VI.22)

The similarity transform is carried out by the subroutine STCM (see appendix D).

B. The Flow Chart

From the flow chart (see next page) the steps in the computational process can be followed. (Fig. VI.1)

1. The input data is read in including all external parameters, initial estimates of the crystal parameters and the values of the tensor operator equivalents required. The input data after conversion is printed out.

2. The matrix elements that are independent of the field are calculated from the matrix in Table III.4 using the values for matrix elements given in Table III.7. (Main Programme, See Appendix A).

3. The remaining field dependent matrix elements are
Fig VI.1. FLOW CHART FOR COMPUTER PROGRAMME
calculated using the components of the measured field values in addition to the data utilised in 2. (RTN 1 See Appendix B).

4. The Hamiltonian matrix formed in 2 and 3 is then diagonalised exactly using the subroutine CEIGEN (Appendix C) which returns eigenenergies and eigenvectors. The difference between the adjacent eigenvalues provides the basis of the least squares sum while the eigenvectors are used in the similarity transform in the next step. The value of DEVIATION printed out is a measure of the fit.

5. The derivative matrix is then transformed to the new basis in which the Hamiltonian is diagonal, see (VI.22). This then allows calculation of DE(I), the derivative of the energy with respect to each parameter, see (VI.17) and the second derivative D2E, see (VI.21). From these the 1st and second derivatives of the least squares sum are formed, D1F(I), see (VI.12) and D2F see (VI.13).

Step 5 is repeated for each parameter in the I = I+1 loop, while the computation of the second derivatives is repeated for all parameters J, with each parameter I in the J = J + 1 loop.

Steps 3 to 5 are then repeated for each of the (N-1) resonant fields at a given orientation during the INDEX = INDEX + 1 loop, which itself is repeated for each of the M orientations in the L = L + 1 loop.

6. As D2F involves summation of both I and J simultaneously as well as a summation over all resonant fields it is not completed till the end of step 5. D2F is then inverted using DMINV (see Appendix E) The parameter correction D(I) can then be calculated see (VI.11),
The new estimate of the parameters is then determined

\[ P(I) = P(I) + D(I) \]  \hspace{1cm} (VI.23)

The standard deviation for each parameter is then calculated together with an estimate of what the mean square deviation will be, using the new parameter values.

7. The results are printed and control returned to the main program where steps 2 to 7 are repeated for the number of iterations specified.

8. The parameters are converted to whatever units are required and any auxiliary calculations with the parameters may also be carried out here.

As a check on the inversion process and the reliability of the parameter values, the \( D2F \) and \( (D2F)^{-1} \) matrices are multiplied using the subroutine \( \text{DGMPRO} \) (see Appendix F, based on IBM Routine \( \text{GMPROD} \)) to see that the product is the unit matrix (see VI.11).
C. The Data Deck

The data cards incorporated in the program are described below.

Card 1:- Columns 1-5, integer right justified, number of orientations = LM.

This programme handles 12, MAIN is dimensioned to 16 but some arrays and formats will need to be redimensioned in RTN 1 and CEIGEN for LM > 12.

Columns 6-10, integer, right justified, number of iterations = ITM.

Card 2:- Columns 1-5, integer, right justified, size of matrix = N
(Degeneracy of ground state). Columns 6-10, floating point number, spin value = . Columns 11-15, integer, right justified, number of parameters = IMAX.

Card 3:- Columns 1-80, User name or identification.

Card 4:- Columns 1-80, Description of Experiment.

Card 5:- Values of THETA for each orientation, Columns 1-5, 6-10,...,76-80.

Card 6:- Values of PHI as for 5.

Card 7:- Values for DPPH, MHz measured at poleface, columns 1-10, 11-20,..., 71-80.

Card 8:- As for 7 when 8 < LM < 16.

Card 9 - 20 (for 12 orientations):- Field values in MHz measured at poleface, entered 7 to a card, order determined as increasing magnitude on Z axis.

Each card represents one orientation, columns 1-10, 11-20,...,71-80.

Card 21:- Columns 1-10, 11-20,...,41-50.

Poleface correction = ADJ = 0.999934, Y-intercept = CADJ = 0.001436.

Corrects field at poleface to field at centre.

Conversion factor = PMHG = 0.234869. Converts proton frequency MHz to kg.

g value DPPH = GDP = 2.00360, g value free electron = GFE = 2.00229.
Cards 22-29 (Number varies):

Matrix elements of the angular momentum tensor operators required.

Left justified floating point numbers in columns 1-10, 11-20, ..., 71-80.

(see Table III.6).

Card 30:  Estimated values of parameters in order shown in Format. Floating point numbers in columns 1-10, 11-20, ..., 71-80.

Card 31:  Remaining parameters or blank card.
D. Rate of Convergence

To indicate the rate of convergence a sample run is shown in Table VI.1, giving the mean square deviation in kgauss.

<table>
<thead>
<tr>
<th>Iteration Number</th>
<th>Mean Square Deviation (kgauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.9190</td>
</tr>
<tr>
<td>2</td>
<td>0.0220</td>
</tr>
<tr>
<td>3</td>
<td>0.0550</td>
</tr>
<tr>
<td>4</td>
<td>0.0022</td>
</tr>
<tr>
<td>5</td>
<td>0.0200</td>
</tr>
<tr>
<td>6</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

Even though the value oscillates it can be seen that the convergence is quite rapid.
CHAPTER VII

RESULTS

When determining the position of the magnetic axes, turning points were found for each resonance line, the mean values and greatest deviation for each line are shown in Table VII.1.

<table>
<thead>
<tr>
<th>LINE</th>
<th>Z-AXIS</th>
<th>Y-AXIS</th>
<th>-X-AXIS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_X$</td>
<td>$\theta_H$</td>
<td>$\theta_X$</td>
</tr>
<tr>
<td>I</td>
<td>81.5 $\pm$ 1.3</td>
<td>351.4 $\pm$ 0.7</td>
<td>84.5 $\pm$ 0.1</td>
</tr>
<tr>
<td></td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.0</td>
<td>$\pm$ 0.0</td>
</tr>
<tr>
<td>II</td>
<td>81.5 $\pm$ 1.3</td>
<td>351.4 $\pm$ 0.7</td>
<td>85.5 $\pm$ 0.5</td>
</tr>
<tr>
<td></td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.1</td>
</tr>
<tr>
<td>III</td>
<td>81.5 $\pm$ 1.2</td>
<td>351.1 $\pm$ 0.7</td>
<td>85.9 $\pm$ 0.5</td>
</tr>
<tr>
<td></td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.1</td>
</tr>
<tr>
<td>IV</td>
<td>81.4 $\pm$ 1.1</td>
<td>351.4 $\pm$ 0.6</td>
<td>86.0 $\pm$ 0.1</td>
</tr>
<tr>
<td></td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.2</td>
</tr>
<tr>
<td>V</td>
<td>Saddle-point</td>
<td>351.4 $\pm$ 0.6</td>
<td>86.0 $\pm$ 0.2</td>
</tr>
<tr>
<td></td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.1</td>
</tr>
<tr>
<td>VI</td>
<td>81.6 $\pm$ 1.2</td>
<td>351.4 $\pm$ 0.8</td>
<td>85.3 $\pm$ 0.1</td>
</tr>
<tr>
<td></td>
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<td>$\pm$ 0.1</td>
<td>$\pm$ 0.2</td>
</tr>
<tr>
<td>VII</td>
<td>81.5 $\pm$ 1.3</td>
<td>351.4 Signal</td>
<td>85.5 $\pm$ 0.5</td>
</tr>
<tr>
<td></td>
<td>$\pm$ 0.1</td>
<td>$\pm$ 0.0</td>
<td>$\pm$ 0.5</td>
</tr>
</tbody>
</table>

Means:

$\bar{\theta}_X = +81.5 \pm 0.1$

$\bar{\theta}_H = +1.2 \pm 0.1$

Error represents the maximum deviation over a series of readings.
As can be seen from the results, the Z and Y axes are well defined but the axis varies over 3 on the magnet scale. A similar variation in one axis of an angular variation plot is observed for gadolinium in a cubic field (Low$^1$). The fact that the X turning points occur at different orientations for each line leads to some uncertainty as to the exact position of the XY plane. This is overcome by using a plane perpendicular to the Z axis that passed through the well defined Y axis. This could lead to a 1° uncertainty for some orientations.

The results of the angular variation carried out in the XZ, YZ and XY planes may be seen plotted in Figs. VII.1, VII.2 and VII.3. Typical spectra with the field directed along each of the magnetic axes in turn are shown in Fig. VII.4, Z axis [0001]; Fig. VII.5a, X axis [12$\bar{1}$0]; Fig VII.5b, Y axis [1010]. The ratio of the line intensities for these spectra is shown in Table VII.2, where they have been normalised to the theoretical ratio which is also included (figures are given to the nearest integer).

<table>
<thead>
<tr>
<th>TABLE VII.2.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
</tr>
<tr>
<td>Z Axis</td>
</tr>
<tr>
<td>Y Axis</td>
</tr>
</tbody>
</table>

For calibration, fields measured at the poleface and the gap centre are recorded in Appendix G. A linear regression analysis was carried out on these values giving a correlation coefficient of 0.9999999921 and a calibration curve of:
\[ H_{\text{centre}} = 0.999934H_{\text{poleface}} + 0.001436 \]  \hspace{1cm} (VII.1)

Proton Magnetometer readings for the resonant fields at a series of selected orientations, are given in Table VII.3. Using the calibration correction the field values have been converted to kilogauss and are presented in Table VII.4 together with the field value of DPPH used to measure the microwave frequency.

The values of the crystal field parameters calculated by the fitting programme are presented in Table VII.5 together with their standard deviations. The calculation was carried through sufficient iterations so that the change in the parameters, \( D(I) = 0 \), to 6 significant figures. In this case 4 iterations were required. A measure of the fit is given by the mean square deviation \( = 7.98 \times 10^{-3} \text{kg} \). which gives a R.M.S. deviation \( = 88 \text{ gauss} \) for 63 resonant fields.
Fig VII.3. ANGULAR VARIATION IN XY PLANE
Fig VII.4 TYPICAL SPECTRUM WITH FIELD PARALLEL TO Z DIRECTION ALONG 0001 AXIS
Fig VII 5 TYPICAL SPECTRUM IN DIRECTION PERPENDICULAR TO Z AXIS

a: ALONG 1210 DIRECTION
b: ALONG 1010 DIRECTION
<table>
<thead>
<tr>
<th>Orientation</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
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<tr>
<td>D.P.P.H.</td>
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<td>35.4821</td>
<td>35.6126</td>
<td>35.6207</td>
<td>35.4850</td>
<td>35.4966</td>
<td>35.5005</td>
<td>35.6090</td>
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<td></td>
<td>± 02</td>
<td>± 05</td>
<td>± 06</td>
<td>± 02</td>
<td>± 03</td>
<td>± 07</td>
<td>± 02</td>
<td>± 04</td>
<td>± 07</td>
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<td>180</td>
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<td>110</td>
<td>71</td>
<td>109</td>
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<td>90</td>
<td>180</td>
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<td>45</td>
<td>90</td>
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<td>180</td>
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<tr>
<td>Line I</td>
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<td>44.2891</td>
<td>17.7120</td>
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<td>± 05</td>
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<td>± 09</td>
<td>± 61</td>
<td>± 18</td>
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<td>± 07</td>
<td>± 01</td>
<td>± 09</td>
<td>± 18</td>
<td>± 09</td>
<td>± 07</td>
</tr>
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<td>30.8949</td>
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<td>± 08</td>
<td>± 05</td>
<td>± 01</td>
<td>± 07</td>
<td>± 04</td>
<td>± 11</td>
<td>± 07</td>
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<tr>
<td>IV</td>
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<td>35.8327</td>
<td>34.8315</td>
<td>35.7279</td>
<td>35.7609</td>
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<td>35.7164</td>
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<td>± 03</td>
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<td>V</td>
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<td>32.2715</td>
<td>40.7652</td>
<td>32.0625</td>
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<td>± 14</td>
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<td>± 26</td>
<td>± 29</td>
<td>± 24</td>
<td>± 37</td>
<td>± 72</td>
<td>±100</td>
<td>± 38</td>
<td>± 18</td>
<td></td>
</tr>
</tbody>
</table>

The error shown represents the maximum deviation over a series of readings.
<table>
<thead>
<tr>
<th>Orientation #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta )</td>
<td>0.0</td>
<td>90.0</td>
<td>90.0</td>
<td>180.0</td>
<td>90.0</td>
<td>70.0</td>
<td>110.0</td>
<td>71.0</td>
<td>109.0</td>
</tr>
<tr>
<td>( \phi )</td>
<td>0.0</td>
<td>90.0</td>
<td>180.0</td>
<td>0.0</td>
<td>45.0</td>
<td>90.0</td>
<td>90.0</td>
<td>180.0</td>
<td>180.0</td>
</tr>
</tbody>
</table>

**TABLE VII.4.**
TABLE VII.5

CRYSTAL FIELD PARAMETERS

\[ g_x = 1.990 \pm 0.005 \]
\[ g_y = 1.991 \pm 0.005 \]
\[ g_z = 1.989 \pm 0.006 \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Gauss</th>
<th>Standard deviation</th>
<th>Parameter</th>
<th>Gauss</th>
<th>((10^{-4} \text{ cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>B_{20}</td>
<td>-534.8</td>
<td>0.1</td>
<td>b_2^0</td>
<td>-655.0</td>
<td>-0.6124</td>
</tr>
<tr>
<td>B_{40}</td>
<td>-3.1</td>
<td>0.5</td>
<td>b_4^0</td>
<td>-11</td>
<td>-0.011</td>
</tr>
<tr>
<td>B_{60}</td>
<td>0.2</td>
<td>0.1</td>
<td>b_6^0</td>
<td>4</td>
<td>+0.004</td>
</tr>
<tr>
<td>B_{43}</td>
<td>1.2</td>
<td>0.6</td>
<td>b_4^3</td>
<td>+27</td>
<td>+0.03</td>
</tr>
<tr>
<td>C_{43}</td>
<td>0.7</td>
<td>0.6</td>
<td>c_4^3</td>
<td>2</td>
<td>+0.001</td>
</tr>
<tr>
<td>B_{63}</td>
<td>-0.1</td>
<td>0.1</td>
<td>b_6^3</td>
<td>-170</td>
<td>0.2</td>
</tr>
<tr>
<td>C_{63}</td>
<td>0.1</td>
<td>0.1</td>
<td>c_6^3</td>
<td>+124</td>
<td>0.1</td>
</tr>
<tr>
<td>B_{66}</td>
<td>-0.06</td>
<td>0.08</td>
<td>b_6^6</td>
<td>-9</td>
<td>-0.009</td>
</tr>
<tr>
<td>C_{66}</td>
<td>-0.05</td>
<td>0.16</td>
<td>c_6^6</td>
<td>-9</td>
<td>-0.008</td>
</tr>
</tbody>
</table>
CHAPTER VIII
DISCUSSION AND CONCLUSION

After examining the data the most obvious point for discussion must be the poor fitting achieved with theoretically calculated energy levels (R.M.S. deviation = 88 gauss). The greatest deviation in the P.M.R. measurements of the resonant fields is \( \pm 0.0100 \) in 29.6985 MHz measured on line 7 which, due to its low intensity, maintains the largest error throughout the experiment. This represents an error of 2.5 gauss or 0.03%. With the exception of the two end lines the error is, for the most part, less than 0.25 gauss. Considering this, together with some degree of misalignment of the crystal, it would not be unreasonable to expect the R.M.S. deviation of the fitting process to be \(< 5\) gauss.

The R.M.S. error is then considerably greater than experimental error which would seem to indicate errors in measurement or orientation of the crystal. However, these data represent a second set of measurements which improved the R.M.S. error from 120 gauss to 88 gauss. As the second set of readings were taken on a different crystal, and the differences could be attributed to the method of defining the XY plane, it would seem that the measurements can be accepted as being accurate. The first set tried to define the XY plane by determining the turning points that occur every 30° (see Fig. VII.3), while the second method is described in chapters V and VII.

It would then appear that the model used in the theoretical calculations should be checked and may need some changes in the terms
included in the spin Hamiltonian. This can best be done by considering all of the information gathered from the system.

1. The fact that the Y axis is well defined and the X axis is not would appear to indicate an inequivalence of X and Y.

2. The angular variation in the YX plane is symmetric about the Y axis with collapse points spread over $35^\circ$ but centred around $55^\circ$ from the Z axis. The angular variation in the XZ plane however is not symmetric about the X axis and collapse points for pairs of lines occur up to $2^\circ$ different on either side of the X axis, which is to be expected as an hydroxyl ion lies in the XZ plane on one side of the X axis but not on the other. This would seem to indicate an inequivalence of X and Y also. In the XY plane the angular variation shows a $60^\circ$ periodicity which is probably associated with the $B_{63}$ as it is the largest trigonal term. This periodicity causes the resonant fields to vary slightly in the X and Y directions up to 40 gauss for some lines (see VII.3).

3. If the behavior of the resonant fields is observed in a cone $\theta = 80^\circ$, $60^\circ$ periodicity is noted. However, by the time $\theta = 70^\circ$ is reached the $60^\circ$ periodicity disappears and is replaced by a $180^\circ$ periodicity. A $180^\circ$ periodicity was also observed for $\theta = 60^\circ$. A complete angular variation around one of these cones has not been made but 3 turning points have been noted $94^\circ$ and $91^\circ$ apart, the discrepancy from $90^\circ$ probably is due to incorrect setting on the crystal rotator. Only a rough check has yet been made, varying the magnet scale but not the crystal.

The fact that a two-fold symmetry exists for the off-axis positions mentioned in 3, seems to suggest the need for the inclusion of some orthorhombic terms in the Hamiltonian, namely $B_{22}$, $B_{42}$ and $B_{44}$. 

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The effect of these terms on the fitting is under investigation at present, and it is hoped that they will prove to be responsible for the present bad fit. Why these effects are found in gadolinium but not in manganese is probably due to the charge compensator associated with the Gd$^{3+}$ ion causing local distortion of the site symmetry.

The intensity ratios in Table VII.2 show reasonable agreement with the theoretical, the fact that they are all below the theoretical values is probably due to increased line width.

The orthorhombic terms gave a fit with R.M.S. error of 91 gauss and so offered no improvement. For an orthorhombic distortion the charge compensator would have to be in a position off the z axis. With the three fold axis of symmetry associated with the site this would produce three sets of spectra due to the three inequivalent sites that the charge compensator could occupy.

The next stage in the investigation will involve the introduction of terms non-linear in magnetic field and also hyperfine and nuclear Zeeman terms.
BIBLIOGRAPHY

17. Ibid, p.46.

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(Cambridge Univ. Press, 1951).


APPENDIX A

4

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REPRODUCED WITH PERMISSION OF THE COPYRIGHT OWNER. FURTHER REPRODUCTION PROHIBITED WITHOUT PERMISSION.
CALL SQLQ (OPT (1, 1), IST (1, IB), IPCTY, 1, JPC (1, J) - 1, IB)

DIM (1) = OPT (1, 1) + OPT (1, J - 1)

CONTINUE

521 IF (IB .LT. J) GO TO 522

522 IF (IB .EQ. J) GO TO 523

523 KLO = IB - (IB + 10) / 2

524 KOS = KLO + J

525 GO TO 526

526 CONTINUE
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APPENDIX C
Subroutine: CEIGEN

Purpose: Compute eigenvalues and eigenvectors of a Hermitean matrix (double precision complex).

Usage: CALL CEIGEN (A, R, N, MV)

Description of parameters:

A - (COMPLEX * 16) original Hermitean matrix, destroyed during computation. Upon return, A is the diagonalized matrix with eigenvalues in ascending order on the diagonal. Compact storage is used, the upper right side of the matrix actually stored: the (I,J) element is the I + (J * J - J)/2 element of A for I < J. For I > J the (I, J) element is the complex conjugate of the (J,I) element, i.e. of the J + (I * I - I)/2 member of A.

R - (COMPLEX *16) the unitary transformation which diagonalizes A. The columns of R are eigenvectors of A ordered as are the eigenvalues.

N - the order (dimension) of A and R

MV - input code:

<table>
<thead>
<tr>
<th>MV</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>compute eigenvalues and eigenvectors</td>
</tr>
<tr>
<td>1</td>
<td>compute eigenvalues only. (R need not be dimensioned but must still appear in calling sequence.)</td>
</tr>
</tbody>
</table>

Method: an extension of the Jacobi method to Hermitean matrices as given, for example in C.-E Froberg, Introduction to Numerical Analysis (Addison-Wesley, 1965) p. 111. The coding parallels that for EIGEN (see publication 360A-OM, p.165).

Programmed by: Wm. E. Baylis, Physics Department, University of Windsor.

Execution time: ~ 0.5 sec CPU on the IBM 360 Model 50 of University of Windsor for N = 4. The time will vary roughly as N^4 but will be less if some off-diagonal elements of A are initially = 0.
COMPUTES DOUBLE PRECISION EIGENVALUES AND EIGENVECTORS UNDER 64
OF THE HERMITIAN MATRIX CA OF DIMENSION N.
USE FOR THE JACOBI METHOD IS USE.
EIGENVALUES ARE STORED IN THE DIAGONAL ELEMENTS OF CA. IF ANY
ORDER, THE EIGENVECTORS ARE STORED COLUMNWISE IN CA IN THE SAME
SEQUENCE.

e. e. baylis. feb 1972.

IMPLICIT REAL*8 (A,B,C,D,E,F,G,H), COMPLEX*16(C)
COMPLEX*16 ONE/(1.000,0.000), ZERO/(0.000,0.000), DCOSJ
REAL*8 COSP, COSP2, COSARS
DIMENSION CA(64), CP(64), CSIMP(2)

CHECK DIMENSION

IF(N-1)1,2,5
1 PRINT 200,N
20 FORMAT('ERROR, ATTEMPT TO DIMENSION EF1331M BY N: ',I16,'! STOP'

EXECUTION!')
STOP
2 IF(NNEQ,1) GO TO 4
CP(I) = ONE
4 RETURN

GENERATE IDENTITY MATRIX

5 RANGE = 1,60-12
IF(NNEQ,1) GO TO 23
10 = I-N
DO 20 J=1,N
10 = 10 + 1
DO 20 T=1,N
20 CONTINUE
C = ZERO
IF(1NEQ,J) CR(I,J) = ONE
20 CONTINUE

COMPUTE INITIAL AND FINAL NORMS

25 ANORM = 0.000
30 Y = 0.000
35 I = 0
60 DO 85 L=1,1
65 DO 85 J=1,1
80 CONTINUE
X = CA(I,J) * COSP + (CA(I,J))
ANORM = ANORM + X
60 CONTINUE
Y = Y + X
80 CONTINUE

35 CONTINUE

AMAX = 1.AIAMAX10000000(AMAX)
ANORM = ANORM / AMAX + AMAX
65 CONTINUE

INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THE

101 INE = 0
105 THE = AMAX
203 AM = THE / DEL0PTION

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C. SORT RELATIVE AND SUBLEVELS

779 100  IF J = i, 
782 784  THEN B(J, i) = B(J, i) + 1
785 786  END IF
787 788  FOR J = 1 TO N
789 790  PRINT ST(J, l), 
791 792  END FOR

C. SORT RELATIVE AND SUBLEVELS
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APPENDIX E

PROGRAM DOUBLE PRECISION CPAM

1. BEGIN

INTEGER M, L, K, N, I, J, I1, I2, I3, I4, I5, I6
C DOUBLE PRECISION A(225), L(15), M(15)

INTEGER (5) SYMBOLOGICAL PRINTER SITE READ (15, 12)

C SEARCH FOR LARGEST ELEMENT

DO 10 I = 1, 225
C
10 K = L(I)
C
20 DO 30 K = 1, N
C
30 Z = Z + 1
C
40 IF (Z = N) GOTO 30
C
50 Z = Z + 1
C
60 RETURN
C
20 CONTINUE
C
C INTERCHANGE ROWS

POLK = POLK + 1
C
DO 70 K = 1, N
C
70 K = K + 1
C
80 DO 90 J = 1, N
C
90 J = J + 1
C
A(K) = A(J)
C
100 RETURN
C
C INTERCHANGE COLUMNS

POLK = POLK + 1
C
DO 110 K = 1, N
C
110 K = K + 1
C
120 DO 130 J = 1, N
C
130 J = J + 1
C
A(K) = A(J)
C
140 RETURN
C
C DIVIDE COLUMNS BY ITERATIVE GROWTH CONTAINED IN YJ

150 IF (SYMBOLOGICAL SITE READ (15, 12)) GOTO 10
C
160 RETURN
C
RETURN
C
180 DO 190 K = 1, N
C
190 K = K + 1
C
200 EXIT
C
END
```
500  DO 10, 40, 10
10  A(I,J) = A(I,J)/B(J)
200  CONTINUE
500  END
```

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APPENDIX F

1. REPROCEDURE (X=100, Y=100)
2. PX=10, PY=10
3. IF (X=100) THEN
   4. IF (Y=100) THEN
      5. GO TO 10
   6. ELSE
      7. GO TO 15
   8. END IF
   9. END IF
10. STOP
11. END

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### APPENDIX G

<table>
<thead>
<tr>
<th>Nominal Field in KG</th>
<th>Pole Face MHz</th>
<th>Centre MHz</th>
<th>Difference MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>19.4761</td>
<td>19.4754</td>
<td>0.0007</td>
</tr>
<tr>
<td>6.0</td>
<td>25.9100</td>
<td>25.9087</td>
<td>0.0013</td>
</tr>
<tr>
<td>7.0</td>
<td>30.1988</td>
<td>30.1975</td>
<td>0.0013</td>
</tr>
<tr>
<td>8.0</td>
<td>34.4924</td>
<td>34.4913</td>
<td>0.0011</td>
</tr>
<tr>
<td>9.0</td>
<td>38.7812</td>
<td>34.7792</td>
<td>0.0020</td>
</tr>
<tr>
<td>10.0</td>
<td>43.0726</td>
<td>43.0707</td>
<td>0.0019</td>
</tr>
<tr>
<td>11.0</td>
<td>47.3530</td>
<td>47.3503</td>
<td>0.0027</td>
</tr>
<tr>
<td>12.0</td>
<td>51.6332</td>
<td>51.6308</td>
<td>0.0024</td>
</tr>
</tbody>
</table>
VITA AUCTORIS

I was born in Belmont, N.S.W., Australia, in 1945, completed Primary Education at Swansea Public School, 1956 and Secondary Education at Belmont High School, 1961. My B.Sc. in Physics was obtained from Newcastle University College in 1964 and my Diploma in Education in 1965. I taught Physics at Wollongong High School, Wollongong, from 1966 - 68 and at Swansea High School during 1969. I taught at W.F. Herman Collegiate, Windsor, Ontario, from 1969 until 1971 and I am at present completing requirements towards my M.Sc. degree at the University of Windsor, Ontario.