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A study of the E.P.R. spectrum of the calcium(OH)2:gadolinium(3+) system

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A STUDY OF THE E.P.R. SPECTRUM OF THE

$$Ca(OH)_2 : Gd^{3+} \text{ SYSTEM}$$

by

Barry James Fox

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ABSTRACT

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 consistant with a trigonal field.

The Spin Hamiltonian

$$H = \beta \, S \cdot g \cdot H + \sum_{n,m} B_{nm} \, T_{nm} \cdot \quad \begin{array}{l} n = 0, 2, 4, 6 \\ m = 0, 3, 6 \end{array}$$

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

$$b_2^o = -655.0; \qquad b_4^o = -11; \qquad b_6^o = +4$$

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

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

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.

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

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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 $Gd^{3+}({}^8S_{7/2})$ 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).

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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.

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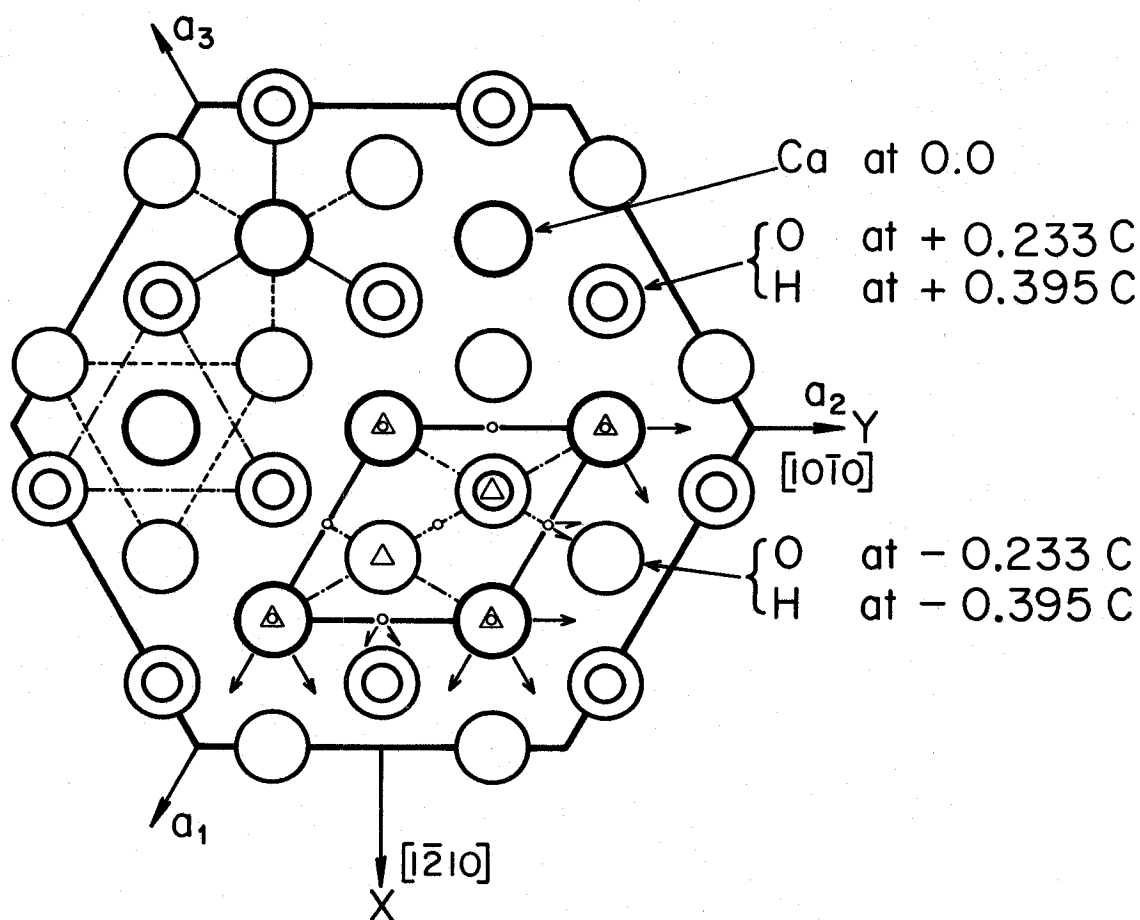
Fig II 1 Structure of Ca(OH)$_2$ projected on the (0001) plane. Some elements of the D$_3^{3}_d$ space group are shown on the unit cell represented by the heavy outline.

    △ 3-fold axis of rotation

    ○ inversion centre

  — – —mirror plane

  ◂——— horizontal 2-fold axis

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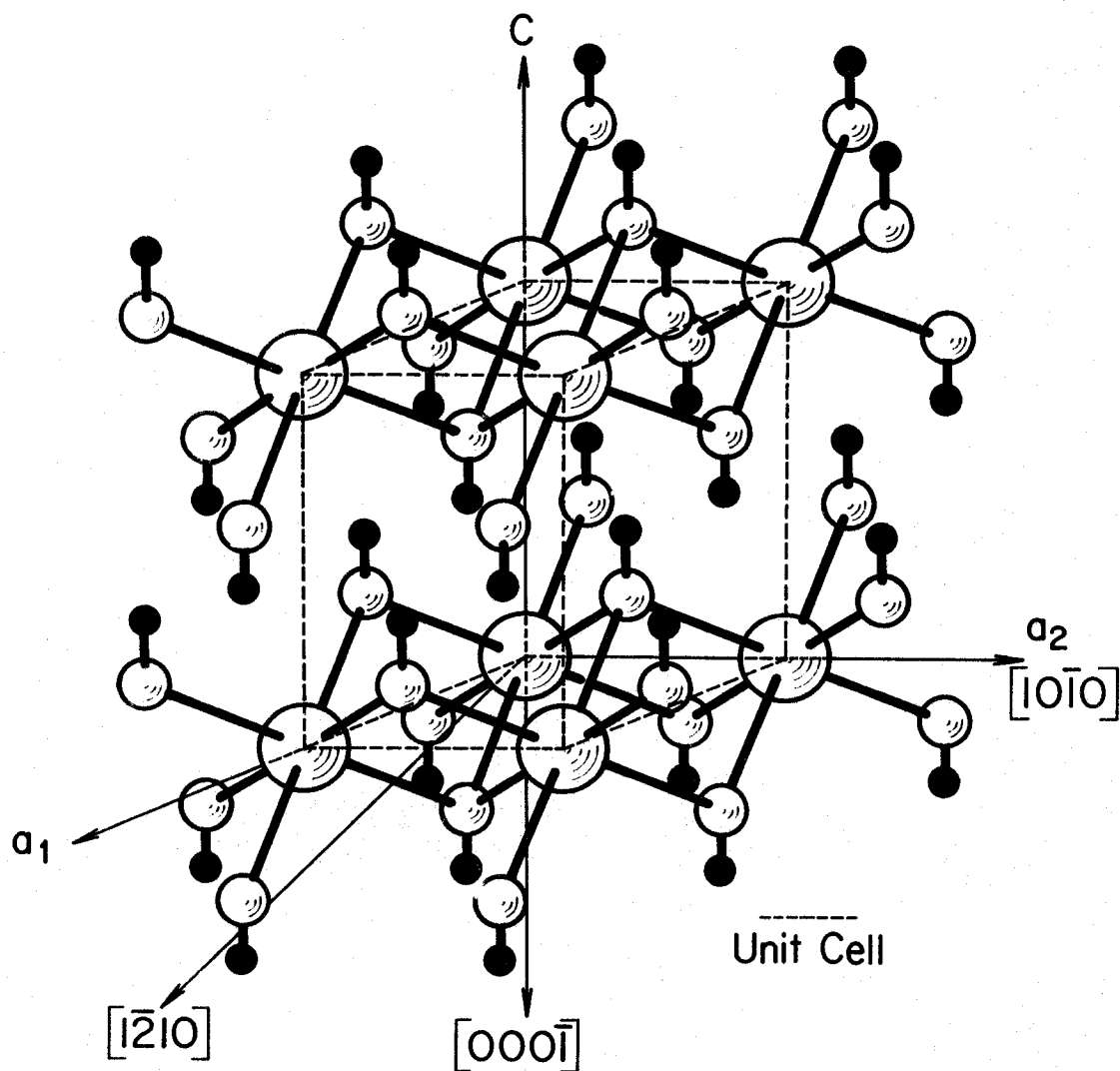
Fig II.2. Three dimensional representation of unit cell ofor $Ca(OH)_2$. The calcium ions appear at the corners of the unit cell, surrounded by an octahedron formed by the oxygen ions in planes above and below. The hydrogen ions (shaded) also lie in basal planes but further from the calcium ions.

TABLE II l^{12}

Unit cell parameter a_o	3.5844 Å
Unit cell parameter c_o	4.8962 Å
Unit cell parameter z_o	0.2330 c_o Å
Structure parameter z_h	0.3950 c_o Å
O-H separation	2.6479 Å

CHAPTER III

THEORY

A. Electron Paramagnetic Resonance

This phenomenon was first reported by Zavoyskiy(1945)[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 β 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 γ such

that the quantum of high frequency energy equals the separation between

levels, i.e.

$$h\gamma = g_s\ \beta H \qquad\qquad (III.1)$$

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

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the system and its accompanying loss of absorption can occur when the rise in temperature caused by the absorption of energy results in an equalization of the two populations.

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

$$E = \pm\, Mg\ \beta H \qquad\qquad\qquad (III.2)$$

where g is the spectroscopic splitting factor and is defined by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L-1)}{2J(J+1)} \qquad (III.3)$$

and the Bohr magneton

$$\beta = \frac{eh}{4\pi mc} \qquad\qquad\qquad (III.4)$$

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,

$$\omega = g\ \frac{e}{2mc}\ H \qquad\qquad\qquad (III.5)$$

for the energies to correspond to the photon energy

$$h\gamma = g\ \beta\ H \qquad\qquad\qquad (III.6)$$

it can be seen that ΔM can only take the values +1 or -1, so the selection rule governing allowed transitions is :

$$\Delta M = \pm 1 \qquad\qquad\qquad \text{(III.7)}$$

B. The Trivalent Gadolinium Ion

Gadolinium has the electronic structure

$$\dots 4f^7 \, 5s^2 \, 5p^6 \, 5d^1 \, 6s^2$$
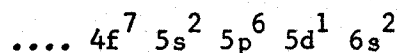
so that the trivalent gadolinium ion has a free ion ground state of $^8S_{7/2}$ in the $4f^7$ configuration. This indicates that the orbital angular momentum is $L=0$. Consequently, the energy levels will be 8-fold spin degenerate, splitting into 8 levels when the degeneracy is completely removed as 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

$$H = T + V_c + V_{so} + V_x + V_{ss} + V_{si} \qquad\qquad \text{(III.8)}$$

where

$$T = \sum_k (p_k^2 / 2m) \qquad\qquad\qquad \text{(III.9)}$$

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

$$V_c = - \sum_k \frac{Ze^2}{r_k} + \sum \frac{e^2}{v_{ij}} \qquad\qquad \text{(III.10)}$$

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

$$V_{so} = \sum_{ij} \lambda_{ij} \, \ell_i \cdot s_j \qquad\qquad \text{(III.11)}$$

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

$$\sum_i \ell_i = \underset{\sim}{L} \text{ and } \sum_j s_j = \underset{\sim}{S} \qquad\qquad \text{(III.12)}$$

so the term becomes

$$V_{so} = \lambda \, \underset{\sim}{L} \cdot \underset{\sim}{S} \qquad\qquad \text{(III.13)}$$

where λ is the spin-orbit coupling constant.

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

$$V_x = - \sum_k e_k \, \Phi(\underset{\sim}{r}_k) \qquad\qquad \text{(III.14)}$$

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

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

where the sum is extended over all pairs of electrons.

The term $V_{s\,\text{I}}$ 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

$$H = \beta\, \underset{\sim}{S}\cdot\underset{\sim}{\tilde{g}}\cdot\underset{\sim}{H} + \sum_{n,m} B_{nm} T_{nm} + \underset{\sim}{S}\cdot\underset{\sim}{\tilde{A}}\cdot\underset{\sim}{I} - g_N \beta_N \underset{\sim}{I}\cdot\underset{\sim}{H} \qquad (III.16)$$

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 $\underset{\sim}{S}$. 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

$$H = \beta\, \underset{\sim}{S}\cdot\underset{\sim}{\tilde{g}}\cdot\underset{\sim}{H} + \sum_{n,m} B_{nm} T_{nm} \qquad (III.17)$$

the terms of which are explained separately in the following paragraphs.

(1)   Zeeman Term

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

$$H = \beta(S_x \; S_y \; S_z) \cdot \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} \cdot \begin{pmatrix} H_x \\ H_y \\ H_z \end{pmatrix}$$

$$H = \beta(g_x \; S_x \; H_x + g_y \; S_y \; H_y + g_z \; S_z \; H_z) \qquad (III.18)$$

$$H = \beta \; g_z \; H_z \; S_z + \beta/2(h_+ S_- + h_- S_+)$$

where

$$h_+ = (g_x H_x + i g_y H_y); \qquad h_- = (g_x H_x - i g_y H_y)$$

$$S_+ = (S_x + i S_y) \qquad ; \qquad S_- = (S_x - i S_y)$$

This can be written in terms of tensor operator equivalents T_{nm}. (See (III.26) and Table III.3

$$H = \beta g_z H_z T_{10} + \beta\left(\frac{h_+}{\sqrt{2}} T_{1-1} - \frac{h_-}{\sqrt{2}} T_{11} \right) \qquad (III.19)$$

(2)   Crystal Field Term

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

$$H_{cr} \equiv \sum_i - e \; V(x_i, y_i, z_i) \qquad (III.20)$$

where the crystal field potential V is a function of the position of the ith 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

$$V = \sum_{i} \sum_{n,m} A_{nm} r^n Y_{nm}(\theta_i, \phi_i) \qquad (III.21)$$

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 $\psi^*\psi$ 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 substititutionally 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

$$
\begin{array}{ll}
m = 0 & \text{Axial} \\
m = \pm 2 & \text{2 fold symmetry} \\
m = \pm 3 & \text{3 fold symmetry} \\
m = \pm 4 & \text{4 fold symmetry} \qquad (III.22) \\
m = \pm 6 & \text{6 fold symmetry}
\end{array}
$$

and by setting

$$A_{no} r^n Y_{no} = U_{no}$$

and

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

then

$$V_{trig.} = U_{20} + U_{40} + U_{60} + U_{43} + U_{63} + U_{66} \qquad \text{(III.23)}$$

Expressing the spherical harmonics in cartesian co-ordinates

TABLE III.1

$$V_{20} = 3z^2 - r^2$$

$$V_{40} = 35z^4 - 30r^2z^2 + 3r^4$$

$$V_{60} = 231z^6 - 315r^2z^4 + 105r^4z^2 - 5r^6$$

$$V_{43} = (x^2 - 3y^3)xz$$

$$V_{63} = (11z^2 - 3r^2)(x^2 - 3y^2)xz$$

$$V_{66} = x^6 - 15x^4y^2 + 15x^2y^4 - y^6$$

where

$$U_{nm} = D_{nm} V_{nm} \qquad \text{(III.24)}$$

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

TABLE III.2

$$D_{20} = \frac{1}{4}\sqrt{\frac{5}{\pi}} A_{20} \qquad\qquad D_{60} = \frac{1}{32}\sqrt{\frac{13}{\pi}} A_{60}$$

$$D_{40} = \frac{3}{16\sqrt{\pi}} A_{40} \qquad\qquad D_{63} = \frac{1}{16}\sqrt{\frac{13.105}{\pi}} |A_{63}|$$

$$D_{43} = \frac{3}{4}\sqrt{\frac{35}{\pi}} |A_{43}| \qquad\qquad D_{66} = \frac{1}{32}\sqrt{\frac{13.21.11}{\pi}} |A_{66}|$$

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

$$\underset{\sim}{L} = 0 \quad \text{then} \quad \underset{\sim}{J} = \underset{\sim}{S} \qquad \text{(III.25)}$$

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.
$$xy \equiv \frac{1}{2} \alpha (J_x J_y + J_y J_x) \qquad \text{(III.26)}$$

where α is a multiplying constant so that

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

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

$$T_{20} = +\sqrt{\frac{1}{6}} \left\{ 3J_z^2 - J(J+1) \right\} \qquad \text{(III.28)}$$

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:

$$H_{cr} = \sum_{nm} B_{nm} T_{nm} \qquad \text{(III.29)}$$
$$n = 2,4,6$$
$$m = 0,\pm 3,\pm 6$$

The spin-Hamiltonian can then be written :

TABLE III.3

$$T_{20} = +\sqrt{\frac{1}{6}}\left[3J_z^2 - J(J+1)\right]$$

$$T_{40} = + \frac{1}{2}\sqrt{\frac{1}{70}}\left[35J_z^4 - 5\left(6J(J+1) - 5\right)J_z^2 + \right.$$
$$\left. + 3\left(J^2(J+1)^2 - 2J(J+1)\right)\right]$$

$$T_{4\pm3} = \mp \frac{1}{2}\sqrt{\frac{1}{2}}\left[J_\pm^3 J_z + J_z J_\pm^3\right]$$

$$T_{60} = + \frac{1}{4}\sqrt{\frac{1}{231}}\left[231J_z^6 - 105\left(3J(J+1)-7\right)J_z^4 + \right.$$
$$+ 21\left(5J^2(J+1)^2 - 25J(J+1) + 14\right)J_z^2$$
$$\left. - 5\left(J^3(J+1)^3 - 8J^2(J+1)^2 + 12J(J+1)\right)\right]$$

$$T_{6\pm3} = \mp \frac{1}{8}\sqrt{\frac{5}{11}}\left[J^3 \pm \{11J_z^2 - \left(3J(J+1) + 59\right)J_z\} + \right.$$
$$\left. + \{11J_z^3 - \left(3J(J+1) + 59\right)J_z\} J_\pm^3\right]$$

$$T_{6\pm6} = \frac{1}{8} J_\pm^6$$

$$T_{1\pm1} = \mp\sqrt{\frac{1}{2}} J_\pm$$

$$T_{10} = + J_z$$

$$H = \beta g_z H_z T_{10} + \beta(\frac{h_+}{\sqrt{2}} T_{1-1} - \frac{h_-}{\sqrt{2}} T_{11}) + B_{20}T_{20} + B_{40}T_{40}$$

$$+ B_{60}T_{60} + (B_{43} + i\, C_{43})T_{43} - (B_{43} - i\, C_{43})T_{4-3}$$

$$+ (B_{63} + i\, C_{63})T_{63} - (B_{63} - i\, C_{63})T_{6-3}$$

$$+ (B_{66} + i\, C_{66})T_{66} + (B_{66} - i\, C_{66})T_{6-6} \qquad \text{(III.30)}$$

F. Calculation of Matrix Elements

(1) The Hamiltonian

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

$$\int \psi_m^* \{T_{NM}\} \psi_m{}' \, d\tau \equiv \langle m|T_{NM}|m'\rangle \qquad \text{(III.31)}$$

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 $0, \pm1, \pm3, \pm6$, 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 III.4.

⟨ \ | ⟩	|+7/2⟩	|+5/2⟩	|+3/2⟩	|+1/2⟩	|−1/2⟩	|−3/2⟩	|−5/2⟩	|−7/2⟩
⟨+7/2|	$\frac{7}{2}h_{\|\|}+7\sqrt{\frac{5}{2}}B_{20}+3\sqrt{70}\,B_{40}+15\sqrt{\frac{21}{11}}B_{60}$	$+\frac{\sqrt{7}}{2}h_-$		$-6\sqrt{70}(B_{43}-iC_{43})-180\sqrt{\frac{7}{11}}(B_{63}-iC_{63})$			$90\sqrt{7}(B_{66}-iC_{66})$	
⟨+5/2|	$+\frac{\sqrt{7}}{2}h_+$	$\frac{5}{2}h_{\|\|}+\sqrt{\frac{3}{2}}B_{20}-39\sqrt{\frac{10}{7}}B_{40}-75\sqrt{\frac{21}{11}}B_{60}$	$+\sqrt{3}\,h_-$		$-12\sqrt{10}(B_{43}-iC_{43})+\frac{630}{\sqrt{11}}(B_{63}-iC_{63})$			$90\sqrt{7}(B_{66}-iC_{66})$
⟨+3/2|		$+\sqrt{3}\,h_+$	$\frac{3}{2}h_{\|\|}-3\sqrt{\frac{3}{2}}B_{20}-9\sqrt{\frac{10}{7}}B_{40}+135\sqrt{\frac{21}{11}}B_{60}$	$+\frac{\sqrt{15}}{2}h_-$				
⟨+1/2|	$-6\sqrt{70}(B_{43}+iC_{43})-180\sqrt{\frac{7}{11}}(B_{63}+iC_{63})$		$+\frac{\sqrt{15}}{2}h_+$	$\frac{1}{2}h_{\|\|}-5\sqrt{\frac{3}{2}}B_{20}+27\sqrt{\frac{10}{7}}B_{40}-75\sqrt{\frac{21}{11}}B_{60}$	$+2h_-$		$+12\sqrt{10}(B_{43}-iC_{43})-\frac{630}{\sqrt{11}}(B_{63}-iC_{63})$	
⟨−1/2|		$-12\sqrt{10}(B_{43}+iC_{43})+\frac{630}{\sqrt{11}}(B_{63}+iC_{63})$		$+2h_+$	$-\frac{1}{2}h_{\|\|}-5\sqrt{\frac{3}{2}}B_{20}+27\sqrt{\frac{10}{7}}B_{40}-75\sqrt{\frac{21}{11}}B_{60}$	$+\frac{\sqrt{15}}{2}h_-$		$+6\sqrt{70}(B_{43}+iC_{43})+180\sqrt{\frac{7}{11}}(B_{63}+iC_{63})$
⟨−3/2|					$+\frac{\sqrt{15}}{2}h_+$	$-\frac{3}{2}h_{\|\|}-3\sqrt{\frac{3}{2}}B_{20}-9\sqrt{\frac{10}{7}}B_{40}+135\sqrt{\frac{21}{11}}B_{60}$	$+\sqrt{3}\,h_-$	
⟨−5/2|	$90\sqrt{7}(B_{66}+iC_{66})$			$+12\sqrt{10}(B_{43}+iC_{43})-\frac{630}{\sqrt{11}}(B_{63}+iC_{63})$		$+\sqrt{3}\,h_+$	$-\frac{5}{2}h_{\|\|}+\sqrt{\frac{3}{2}}B_{20}-39\sqrt{\frac{10}{7}}B_{40}-75\sqrt{\frac{21}{11}}B_{60}$	$+\frac{\sqrt{7}}{2}h_-$
⟨−7/2|		$90\sqrt{7}(B_{66}+iC_{66})$			$+6\sqrt{70}(B_{43}-iC_{43})+180\sqrt{\frac{7}{11}}(B_{63}-iC_{63})$		$+\frac{\sqrt{7}}{2}h_+$	$-\frac{7}{2}h_{\|\|}+7\sqrt{\frac{5}{2}}B_{20}+3\sqrt{70}\,B_{40}+15\sqrt{\frac{21}{11}}B_{60}$

Where the crystal field parameters are related to the conventional parameters b_n^m by :

<div align="center">

TABLE III.5.

</div>

$$b_2^o = \sqrt{\frac{3}{2}}\, B_{20} \qquad b_4^o = 3\sqrt{\frac{10}{7}}\, B_{40} \qquad b_6^o = \frac{315}{\sqrt{231}}\, B_{60}$$

$$b_4^3 = 15\sqrt{2}\, B_{43} \qquad b_6^3 = \frac{315}{2}\sqrt{\frac{5}{11}}\, B_{63} \qquad b_6^6 = \frac{315}{2}\, B_{66}$$

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

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 III.7

$$DH(GX) = -\frac{T_{11}}{2} H_x \qquad\qquad DH(GY) = i\frac{T_{11}}{2} H_y \qquad 1$$

$$DH(GZ) = T_{10} H_z \qquad\qquad DH(B20) = T_{20}$$
$$DH(B40) = T_{40} \qquad\qquad DH(B60) = T_{60} \qquad 0$$

$$DH(B43) = T_{43} \qquad\qquad DH(C43) = i\, T_{43} \qquad 3$$
$$DH(B63) = T_{63} \qquad\qquad DH(C63) = i\, T_{63}$$

$$DH(B66) = T_{66} \qquad\qquad DH(C66) = i\, T_{66} \qquad 6$$

TABLE III.6.

	J	J_z	Matrix Element		J	J_z	Matrix Element
	7/2	-7/2	.-3.500000D 00		7/2	-7/2	8.573214D 00
	7/2	-5/2	-2.500000D 00		7/2	-5/2	1.224745D 00
	7/2	-3/2	-1.500000D 00		7/2	-3/2	-3.674235D 00
$T_{10}(7/2)$	7/2	-1/2	-5.000000D-01	$T_{20}(7/2)$	7/2	-1/2	-6.123724D 00
	7/2	1/2	5.000000D-01		7/2	1/2	-6.123724D 00
	7/2	3/2	1.500000D 00		7/2	3/2	-3.674235D 00
	7/2	5/2	2.500000D 00		7/2	5/2	1.224745D 00
	7/2	7/2	3.500000D 00		7/2	7/2	8.573214D 00
	7/2	-7/2	2.509980D 01		7/2	-7/2	2.072548D 01
	7/2	-5/2	-4.661393D 01		7/2	-5/2	-1.036274D 02
	7/2	-3/2	-1.075706D 01		7/2	-3/2	1.865293D 02
$T_{40}(7/2)$	7/2	-1/2	3.227118D 01	$T_{60}(7/2)$	7/2	-1/2	-1.036274D 02
	7/2	1/2	3.227118D 01		7/2	1/2	-1.036274D 02
	7/2	3/2	-1.075706D 01		7/2	3/2	1.865293D 02
	7/2	5/2	-4.661393D 01		7/2	5/2	-1.036274D 02
	7/2	7/2	2.509980D 01		7/2	7/2	2.072548D 01
	7/2	-7/2	5.019960D 01		7/2	-7/2	-1.870829D 00
$T_{43}(7/2)$	7/2	-5/2	3.794733D 01		7/2	-5/2	-2.449490D 00
and	7/2	-3/2	0.0	$T_{11}(7/2)$	7/2	-3/2	-2.738613D 00
$(-1)T_{4-3}(7/2)$	7/2	-1/2	-3.794733D 01	and	7/2	-1/2	-2.828427D 00
	7/2	1/2	-5.019960D 01	$(-1)T_{1-1}(7/2)$	7/2	1/2	-2.738613D 00
					7/2	3/2	-2.449490D 00
					7/2	5/2	-1.870829D 00
	7/2	-7/2	1.435904D 02				
$T_{63}(7/2)$	7/2	-5/2	-1.899522D 02	$T_{66}(7/2)$	7/2	-7/2	2.381176D 02
and	7/2	-3/2	0.0	and			
$(-1)T_{6-3}(7/2)$	7/2	-1/2	1.899522D 02	$(-1)T_{6-6}(7/2)$	7/2	-5/2	2.381176D 02
	7/2	1/2	-1.435904D 02				

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 VA 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.

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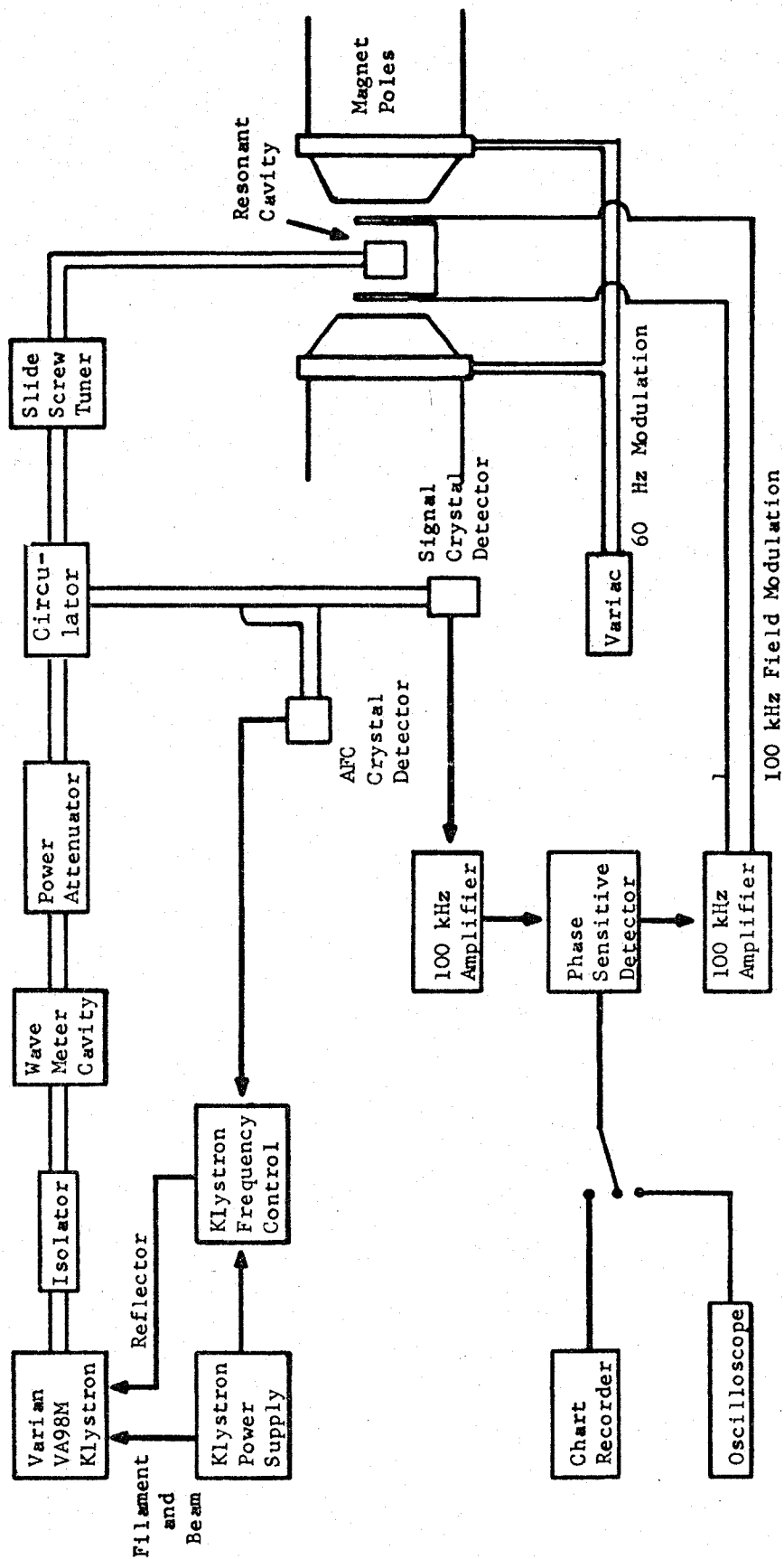
Fig. IV.1. BLOCK DIAGRAM OF K BAND SPECTROMETER

(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 H_z 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[21]. 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 KGauss.

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

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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° 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° interval for the magnetic field direction

moving in each of these planes in turn, XY(0001), XZ(1$\bar{2}$10) and YZ(10$\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

Range

Resonator Number	X-Band Unit MHz	K-Band Unit MHz
5	10.8 - 16.1	13.1 - 22.5
6	14.5 - 21.7	18.7 - 32.0
7	20.0 - 30.0	31.4 - 56.3
8		34.5 - 61.5

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

$$h\gamma = g_P \beta_N H$$

$$H = \frac{h}{g_P \beta_N} \gamma \qquad\qquad (V.1)$$

$$H(KGauss) = 0.234869\ \gamma(MHz)$$

where   H is magnetic field strength

         h is Planck's constant

g_P is the proton g value

β_N is the nuclear magneton

γ 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 α, α'-diphenyl-β-picryl hydrazyl was included with the sample to act as a marker to measure the microwave frequency using the relation

$$h\gamma = g_D \, \beta \, H_D$$
$$\gamma = \frac{g_D \beta}{h} \, H_D \qquad (V.2)$$

where γ is the microwave frequency

g_D is DPPH g value $= 2.0036$

H_D is the field value of the DPPH resonance.
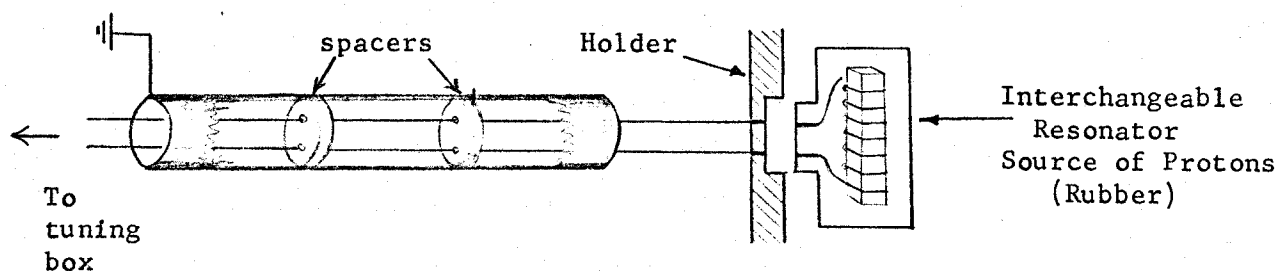
Fig. V.1.

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.[19]. 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[22] is obtained analytically from following condition on the Taylor's series expansion.

$$f(\chi_n + h) = f(\chi_n) + h \cdot f'(\chi_n) + \frac{h^2}{2!} f''(\chi_n) + \ldots = 0 \qquad (VI.1)$$

where χ_n is an approximation of the root of the equation. This can be written in partial derivative form as:

$$\frac{\partial}{\partial \chi_n} f(\chi_n + h) = \frac{\partial}{\partial \chi_n} f(\chi_n) + h \cdot \frac{\partial}{\partial \chi_n} f'(\chi_n) + \ldots = 0 \qquad (VI.2)$$

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 ($i = 1, 2, \ldots I_{max}$), the experimentally measured magnetic field values B, and other experimental parameters necessary

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such as orientation $\hat{\underline{k}}$ 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

$$H = (p_1, p_2, \ldots p_{I_{max}}, \underline{B}, \hat{\underline{k}}, T, \ldots)$$ (VI.3)

The Hamiltonian is represented in an n-dimensional basis $\{|\alpha>\}$.
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

$$<\alpha|H|\beta>$$ (VI.4)

$$<\alpha|\partial H/\partial p_i|\beta>$$ (VI.5)

$$<\alpha|\partial^2 H/\partial p_i \partial p_j|\beta>$$ (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 $(\underline{B}, \hat{\underline{k}}, T, \ldots)$ (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 $\{|i>\}$, (in terms of the original set
$\{|\alpha>\}$, $|i> = \Sigma_\alpha |\alpha> < \alpha|i>$) is then obtained in which the Hamiltonian
is diagonal

$$<i|H|j> = \delta_{ij} E_i$$ (VI.7)

The difference between one adjacent pair of eigenenergies
$(E_{k_1} - E_{k_2})$ will correspond to the transition energy experimentally deter-
mined from measurement of the microwave frequency ν_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:

$$\{(E_{k_1} - E_{k_2}) - \nu_k\}^2 \qquad (VI.8)$$

$$= \{(E_{k_1} - E_{k_2}) - \frac{g_D H_D}{gs}\}^2 \qquad (VI.9)$$

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 free = number of transitions - 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 δ is

$$\frac{\partial}{\partial p_i} f(p + \delta) \approx \frac{\partial}{\partial p_i} f(p) + \sum_j \frac{\partial^2}{\partial p_i \partial p_j} f(p) \delta_j = 0 \qquad (VI.10)$$

The solution is:

$$\delta_i = - \sum_j M_{ij} \frac{\partial}{\partial p_j} f(p) \qquad (VI.11)$$

where $((M_{ij}))$ is the inverse of $((\dfrac{\partial^2}{\partial P_i \, \partial P_j} \, f(\underset{\sim}{p})))$

and

$$\sum_j M_{ij} \frac{\partial^2}{\partial P_j \, \partial P_i'} \, f(\underset{\sim}{p}) = \delta_{ii'}$$

The inversion is carried out by the subroutine DMINV (see appendix). The value of δ_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.

$$\frac{\partial f}{\partial P_i} = \frac{\partial}{\partial P_i} \frac{\Sigma_k \{ (E_{k_1} - E_{k_2}) - \dfrac{g_D \, H_D}{g_D} \}^2}{Nfree}$$

$$= 2 \sum_k (\frac{\partial E_{k_1}}{\partial P_i} - \frac{\partial E_{k_2}}{\partial P_i}) \frac{\{ (E_{k_1} - E_{k_2}) - \dfrac{g_D \, H_D}{g_s} \}}{Nfree} \qquad \text{(VI.12)}$$

and

$$\frac{\partial^2 f}{\partial P_i \, \partial P_j} = 2 \sum_k \left\{ (\frac{\partial E_{k_1}}{\partial P_i} - \frac{\partial E_{k_2}}{\partial P_i})(\frac{\partial E_{k_1}}{\partial P_j} - \frac{\partial E_{k_2}}{\partial P_j}) \right.$$

$$\left. - (\frac{\partial^2 E_{k_1}}{\partial P_i \, \partial P_j} - \frac{\partial^2 E_{k_2}}{\partial P_i \, \partial P_j}) \frac{\{ (E_{k_1} - E_{k_2}) - \dfrac{g_D H_D}{g_s} \}}{Nfree} \right\} \qquad \text{(VI.13)}$$

where

$$\frac{\partial E_k}{\partial P_i} = \lim_{\delta_i \to 0} \{ E_k \frac{(\underset{\sim}{p} + \delta_i \, \hat{\underset{\sim}{i}}) - E_k(\underset{\sim}{p})}{\delta_i} \} \qquad \text{(VI.14)}$$

where $\hat{\underset{\sim}{i}}$ is a unit vector in i-dimensional parameterspace and where

$E_k(\underset{\sim}{p} + \delta_i \hat{i})$ is the eigenenergy (corresponding to $E_k(\underset{\sim}{p})$ of the Hamiltonian $H(\underset{\sim}{p} + \delta_i \hat{i})$ to first order in δ_i

$$H(\underset{\sim}{p} + \delta_i \hat{i}) \simeq H(\underset{\sim}{p}) + \frac{\partial H(\underset{\sim}{p})}{\partial P_i} \partial_i \qquad (VI.15)$$

Using perturbation theory the eigenenergy can also be expressed to first order in δ_i

$$E_k(\underset{\sim}{p} + \delta_i \hat{i}) = E_k(\underset{\sim}{p}) + \langle k | \frac{\partial H}{\partial P_i} | k \rangle \delta_i \qquad (VI.16)$$

and consequently

$$\frac{\partial E_k}{\partial P_i} = \langle k | \frac{\partial H}{\partial P_i} | k \rangle \qquad (VI.17)$$

Similarly

$$\frac{\partial^2 E_k}{\partial P_i \partial P_i} = \lim_{\delta_i, \delta_j \to 0} \frac{E(\underset{\sim}{p} + \delta_i \hat{i} + \delta_j \hat{j}) - E(p + \delta_i \hat{i}) - E(p + \delta_j \hat{j}) + E(\underset{\sim}{p})}{\delta_i \delta_j} \qquad (VI.18)$$

Now to second order in δ's

$$H(\underset{\sim}{p} + \delta_i \hat{i} + \delta_j \hat{j}) = H(\underset{\sim}{p}) + \frac{\partial H}{\partial P_i} \delta_j + \frac{\partial^2 H}{\partial P_i \partial P_j} \delta_i \delta_j +$$

$$+ \frac{\partial H}{\partial P_j} \delta_j + \frac{1}{2}(\frac{\partial^2 H}{\partial P_i^2} \delta_i^2 + \frac{\partial^2 H}{\partial P_j^2} \delta_j^2)$$

$$= H(\underset{\sim}{p}) + V \qquad (VI.19)$$

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

$$E(\underline{p} + \delta_i \hat{\imath} + \delta_j \hat{\jmath}) = E(\underline{p}) + \langle k|V|k \rangle + \sum_{\ell \neq k} \frac{\langle k|V|\ell \rangle \langle \ell|V|k \rangle}{E_k - E_\ell} \qquad \text{(VI.20)}$$

Thus

$$\frac{\partial^2 E}{\partial P_i \partial P_j} = \langle k|\frac{\partial^2 H}{\partial P_i \partial P_j}|k \rangle + 2 \sum_{\ell \neq k} \frac{\langle k|\frac{\partial H}{\partial P_i}|\ell \rangle \langle \ell|\frac{\partial H}{\partial P_i}|k \rangle}{E_k - E_\ell} \qquad \text{(VI.21)}$$

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

$$\langle k|M|\ell \rangle = \sum_{\alpha, \beta} \langle k|\alpha \rangle \langle \alpha|M|\beta \rangle \langle \beta|\ell \rangle \qquad \text{(VI.22)}$$

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

MAIN

RTN 1

Read all data
Orientations (LM),
Iterations (ITM), Matrix
   size, Spin Value,
Parameters Orientation
   (θ, ϕ), DPPH Field,
Magnetic Field value
(INDEX), Conversion
factors, Values of Tensor
Operator Equivalents
Initial Values of Para-
meters

Correct and convert field
values

Print Input Data

Initialize matrices, A,B,
H.DH, Calculate field
independent matrix elements

IT = IT+1

CALL RTN 1

Calculate parameter
Values in required units

Initialize D1F, D2F
Calculate Experimental
ENERGY DIFFERENCE

Calculate Field Components
Compute remaining elements
H(IAB); DH(IAB,I)

L = L+1

CALL CEIGEN
Diagonalize Complex Matrix
H

INDEX = INDEX + 1

Obtain Eigenvalues,
Eigenvectors, Energy
differences.
DEVIATION = Theoretical -
              Exptl.

Transform DH to new basis

I=I+1

COMPUTE DE(I), D1F, D2F, D2E
Derivative matrices in
new basis

J=J+1

CALL DMINV
INVERT D2F

CALCULATE Parameter
correction D(I)
$D(I) = -D2F^{-1}.D1F(I)$

Calculate new value for
parameter $p_i = p_i + \delta_i$,
Standard deviation σ_i
and new mean square
deviation

Print Results

current variables

IT   = iteration #

L   = orientation #

INDEX = Field value #

I   = Parameter #

J   = Parameter #

IAB   = Matrix element #
         (compact storage)

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

$$P(I) = P(I) + D(I) \qquad\qquad (VI.23)$$

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 DGMPRO (see Appendix F, based on IBM Routine GMPROD)[25] 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 <u>orientations</u> = 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 <u>iterations</u> = ITM.

Card 2:- Columns 1-5, integer, right justified, <u>size of matrix</u> = N

(Degeneracy of ground state). Columns 6-10, floating point number,

<u>spin value</u> = . Columns 11-15, integer, right justified, <u>number of</u>

<u>parameters</u> = IMAX.

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

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

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

Card 6:- Values of <u>PHI</u> as for 5.

Card 7:- Values for <u>DPPH</u>, 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):- <u>Field values</u> 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.

<u>Poleface correction</u> = ADJ = 0.999934, <u>Y-intercept</u> = CADJ = 0.001436.

Corrects field at poleface to field at centre.

<u>Conversion factor</u> = PMHG = 0.234869. Converts proton frequency MHz to kg.

g value <u>DPPH</u> = GDP = 2.00360, g value <u>free electron</u> = 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:- <u>Estimated</u> values of <u>parameters</u> 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 VI.1

Iteration Number	Mean Square Deviation (kgauss)
1	0.9190
2	0.0220
3	0.0550
4	0.0022
5	0.0200
6	0.0006

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 VII.1

LINE	Z-AXIS		Y-AXIS		-X-AXIS	
	θ_X	θ_H	θ_X	θ_H	θ_X	θ_H
I	81.5 ± 0.1	+ 1.3 ± 0.0	351.4 ± 0.0	- 0.7 ± 0.0	84.5 ± 0.1	-87.8 ± 0.0
II	81.5 ± 0.0	+ 1.3 ± 0.1	351.4 ± 0.0	- 0.7 ± 0.1	85.5 ± 0.5	-89.9 ± 0.0
III	81.5 ± 0.1	+ 1.2 ± 0.1	351.1 ± 0.1	- 0.7 ± 0.0	85.9 ± 0.1	-90.7 ± 0.0
IV	81.4 ± 0.1	+ 1.1 ± 0.1	351.4 ± 0.0	- 0.6 ± 0.2	86.0 ± 0.1	-88.6 ± 0.0
V	Saddle-point		351.4 ± 0.1	- 0.6 ± 0.1	86.0 + 0.2	-89.2 ± 0.1
VI	81.6 ± 0.0	+ 1.2 ± 0.1	351.4 ± 0.1	- 0.8 ± 0.2	85.3 ± 0.1	-91.1 ± 0.2
VII	81.5 ± 0.1	+ 1.3 ± 0.1	351.4 ± 0.0	Signal too small	85.5 ± 0.5	-89.9 ± 0.1

Means:

		Z-Axis	Y-Axis	-X-Axis
$\overline{\theta}_X$	=	+ 81.5 ± 0.1	+ 351.4 ± 0.3	+ 85.7 ± 1.2
$\overline{\theta}_H$	=	+ 1.2 ± 0.1	- 0.7 ± 0.2	- 89.6 ± 1.8

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 $[1\bar{2}10]$; Fig VII.5b, Y axis $[10\bar{1}0]$. 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 VII.2.

Theoretical	7 : 12 : 15 : 16 : 15 : 12 : 7
Z Axis	4 : 8 : 12 : 16 : 12 : 10 : 5
Y Axis	2 : 6 : 11 : 16 : 11 : 7 : 4
X Axis	3 : 7 : 13 : 16 : 10 : 6 : 2

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:

$$H_{centre} = 0.999934 H_{poleface} + 0.001436 \qquad (VII.1)$$

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 $= 7.98 \times 10^{-3} kg$. which gives a R.M.S. deviation $= 88$ gauss for 63 resonant fields.
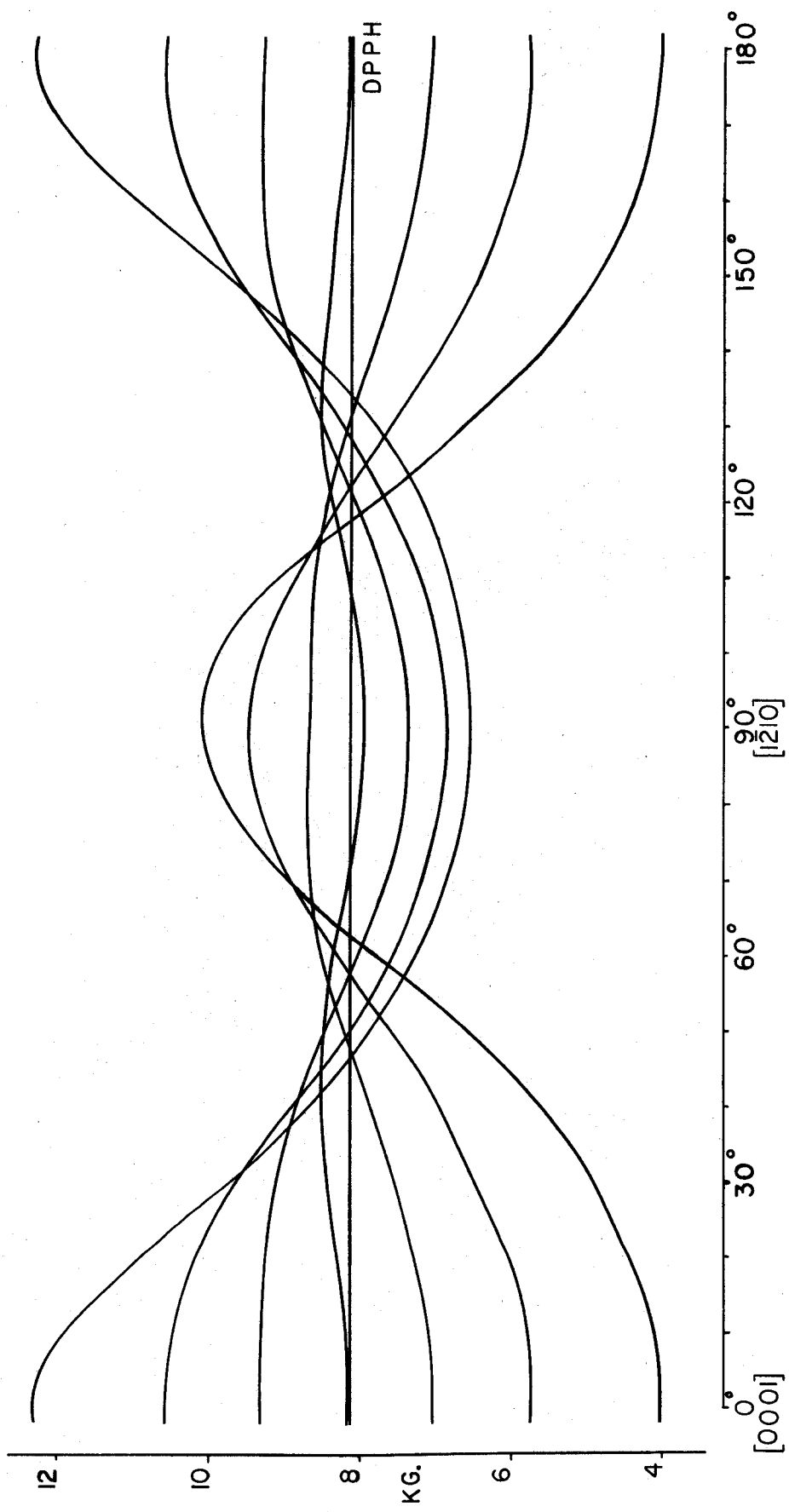
ANGULAR VARIATION IN XZ PLANE

Fig. VII.1.

DPPH
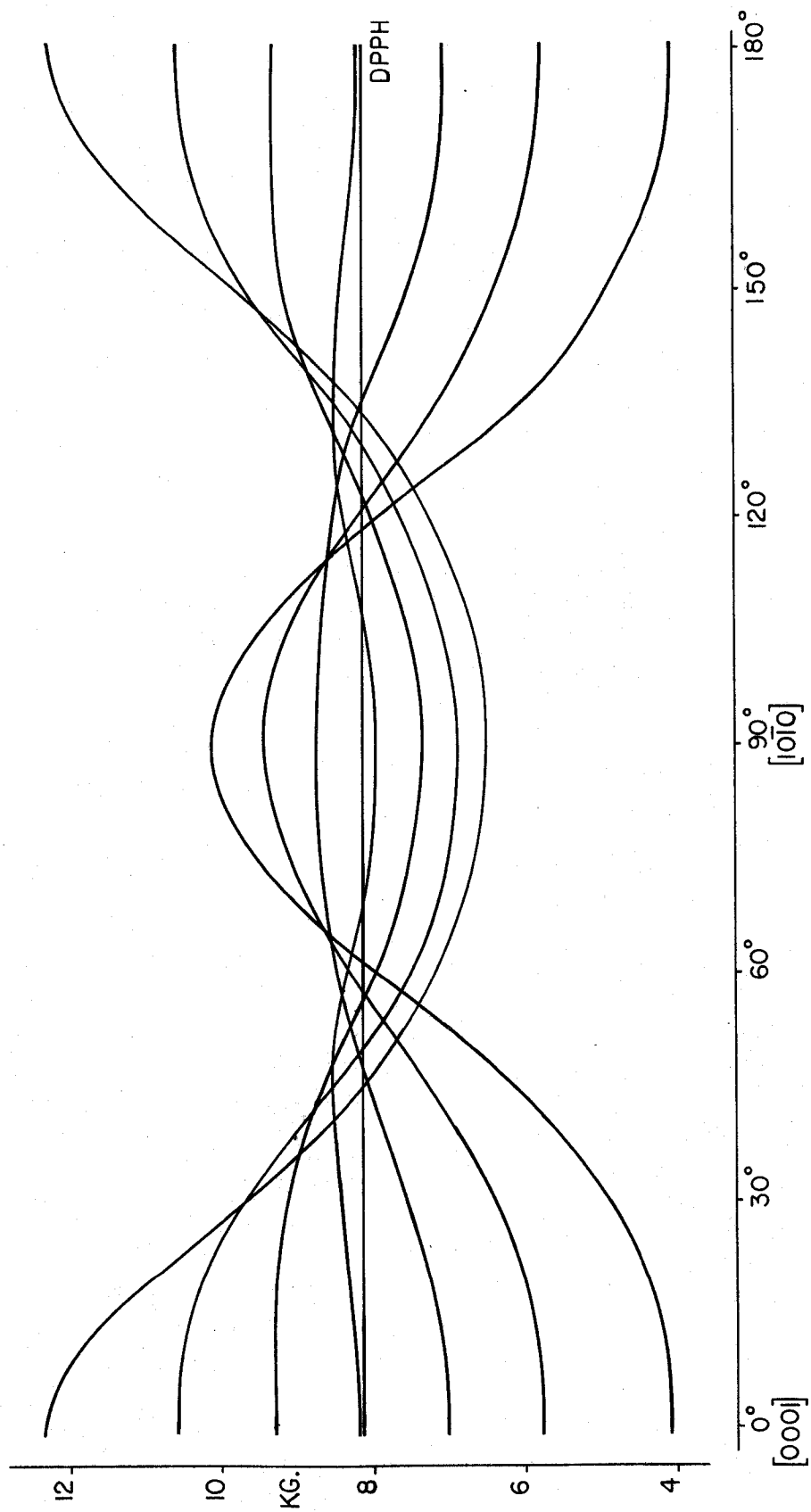
ANGULAR VARIATION IN ZY PLANE

Fig. VII 2
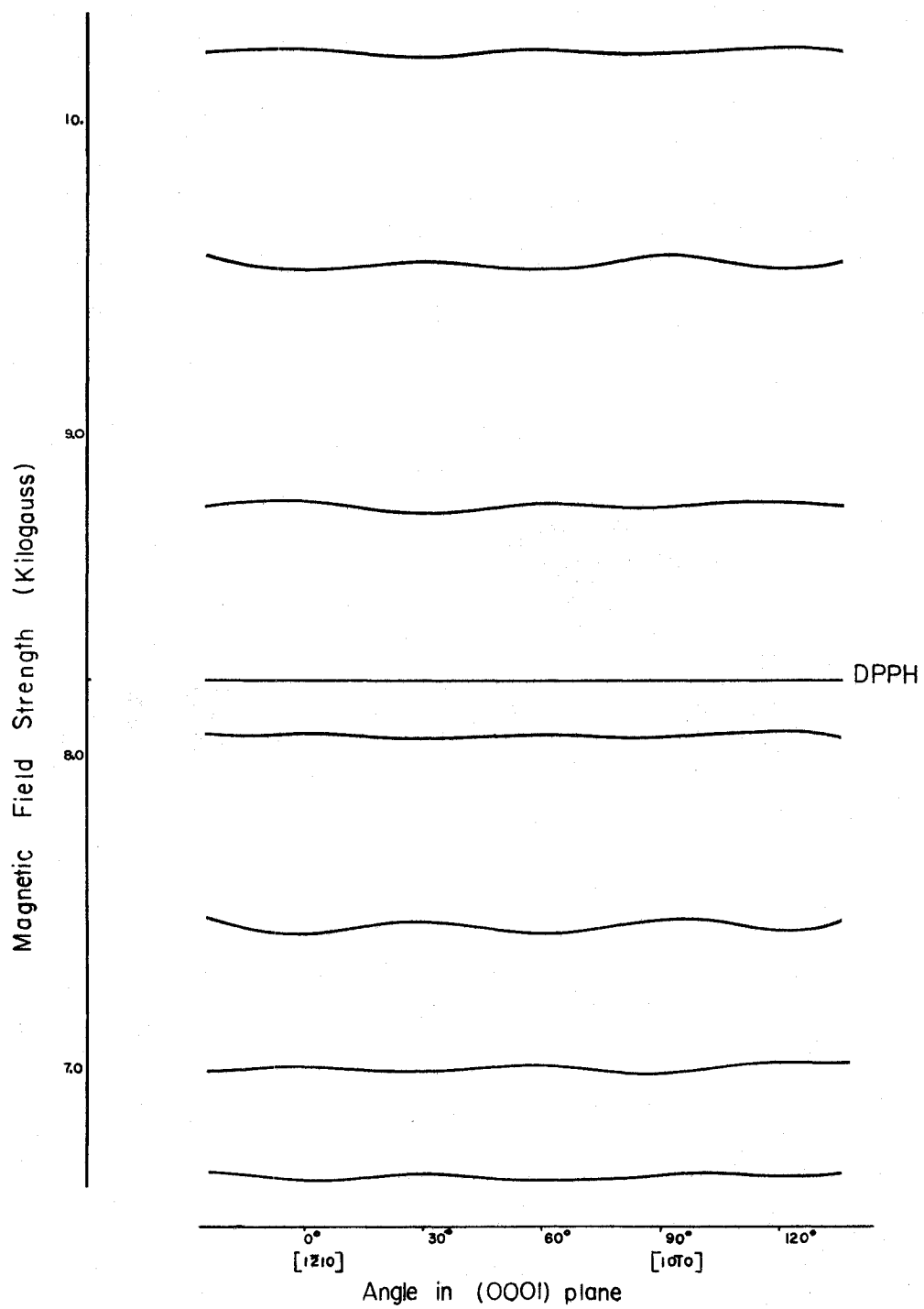
Fig. VII.3. ANGULAR VARIATION IN XY PLANE
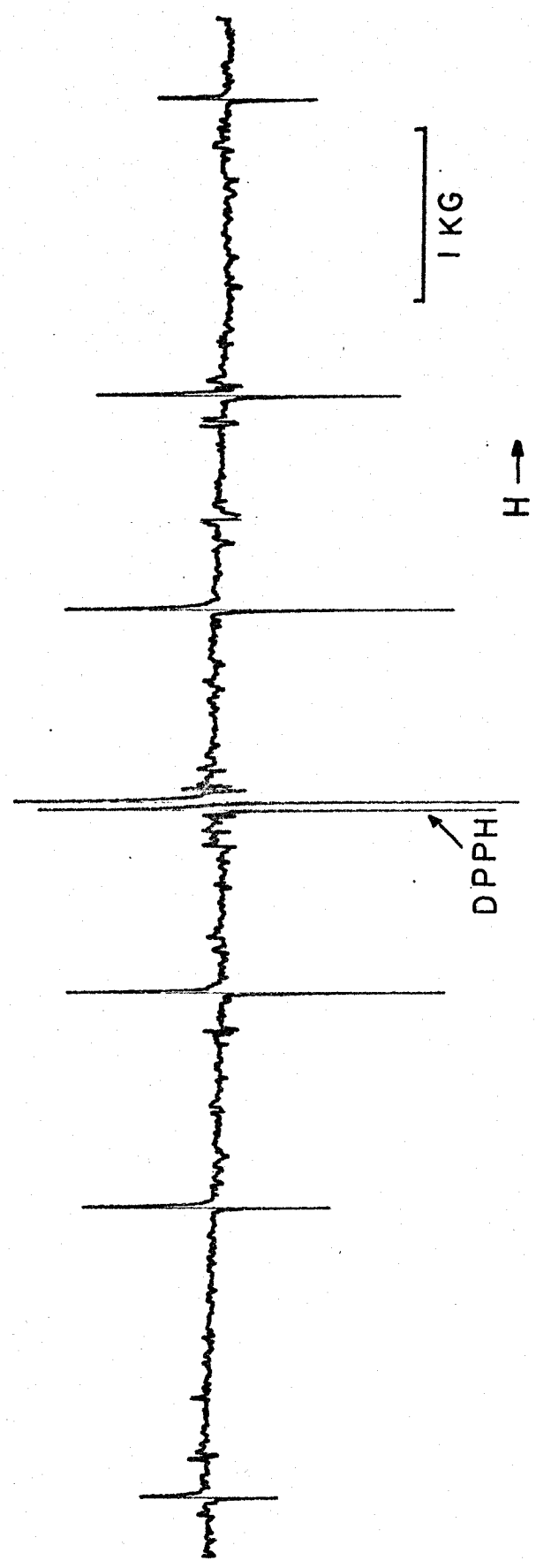
Fig VII.4 TYPICAL SPECTRUM WITH FIELD PARALLEL TO Z DIRECTION ALONG 0001 AXIS
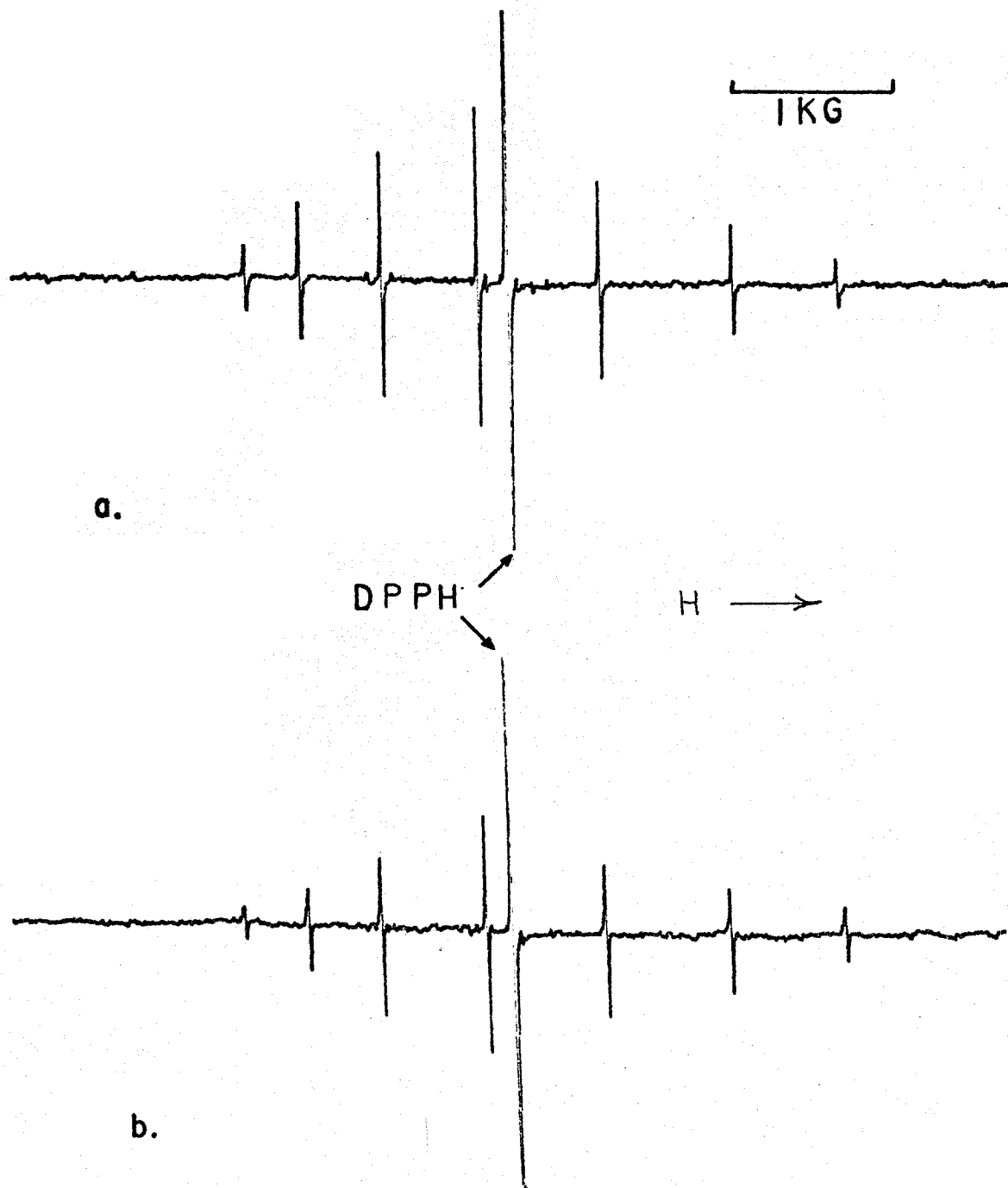
Fig VII 5 TYPICAL SPECTRUM IN DIRECTION PERPENDICULAR TO Z AXIS

a: ALONG 1̄2̄10 DIRECTION

b: ALONG 101̄0 DIRECTION

TABLE VII.3

PROTON MAGNETOMETER FREQUENCIES (MHz)

Orientation	1	2	3	4	5	6	7	8	9
D.P.P.H.	35.6104 ± 02	35.4821 ± 05	35.6126 ± 06	35.6207 ± 02	35.4850 ± 03	35.4966 ± 07	35.5005 ± 02	35.6090 ± 04	35.6146 ± 07
θ	0	90	90	180	90	70	110	71	109
ϕ	0	90	180	0	45	90	90	180	180
Line I	17.6950 ± 26	44.2855 ± 16	44.2891 ± 03	17.7120 ± 05	44.2542 ± 23	39.5481 ± 09	39.8836 ± 61	41.4346 ± 18	39.9501 ± 41
II	25.2823 ± 08	41.2347 ± 02	41.5487 ± 01	25.2944 ± 07	41.3294 ± 07	38.7770 ± 09	38.9431 ± 18	39.6242 ± 09	39.4626 ± 07
III	30.8824 ± 07	38.0060 ± 18	38.0333 ± 08	30.8949 ± 05	37.9579 ± 01	37.6495 ± 07	37.6844 ± 04	37.7864 ± 11	37.8568 ± 03
IV	35.8181 ± 03	34.7535 ± 09	35.8327 ± 05	34.8315 ± 13	35.7279 ± 07	35.7609 ± 10	35.7052 ± 13	35.5234 ± 12	35.7164 ± 05
V	40.7538 ± 02	31.9833 ± 05	32.2715 ± 04	40.7652 ± 03	32.0625 ± 05	33.4328 ± 14	33.3322 ± 06	33.2623 ± 09	33.4136 ± 04
VI	46.3503 ± 05	30.0876 ± 14	30.1023 ± 09	46.3610 ± 07	30.0395 ± 10	31.4862 ± 21	31.3851 ± 09	31.1551 ± 19	31.1828 ± 09
VIII	53.9340 ± 26	28.5000 ± 30	28.6804 ± 29	53.9344 ± 24	28.5351 ± 37	29.7891 ± 72	29.6985 ±100	29.3322 ± 38	29.9654 ± 18

The error shown represents the maximum deviation over a series of readings.

Orientation #	1	2	3	4	5	6	7	8	9
D.P.P.H.	8.36323	8.33310	8.36374	8.36565	8.33378	8.33650	8.33742	8.36290	8.36421
θ	0.0	90.0	90.0	180.0	90.0	70.0	110.0	71.0	109.0
ϕ	0.0	90.0	180.0	0.0	45.0	90.0	90.0	180.0	180.0
Line I	4.15607	10.40094	10.40179	4.16006	10.39359	9.28835	9.35732	9.73140	9.38276
II	5.93797	9.68445	9.75819	5.94082	9.70669	9.10725	9.14626	9.30622	9.26827
III	7.25318	8.92618	8.93259	7.25611	8.91488	8.84245	8.85065	8.87461	8.89114
IV	8.41234	8.16232	8.18094	8.41549	8.15631	8.39891	8.38557	8.34313	8.38846
V	9.57146	7.51173	7.57941	9.57419	7.53033	7.85215	7.82852	7.81203	7.84764
VI	10.88587	7.06652	7.06997	10.88838	7.05522	7.39498	7.37124	7.31722	7.32373
VII	12.66695	6.69366	6.73603	12.66702	6.70191	6.99679	6.97513	6.88911	7.03782

TABLE VII.4.

TABLE VII.5

CRYSTAL FIELD PARAMETERS

$$g_x = 1.990 \pm 0.005$$

$$g_y = 1.991 \pm 0.005$$

$$g_z = 1.989 \pm 0.006$$

				Units	
Parameter	Gauss	Standard deviation	Parameter	Gauss	(10^{-4}cm^{-1})
B_{20}	-534.8	0.1	b_2^o	-655.0	-0.6124
B_{40}	-3.1	0.5	b_4^o	-11	-0.011
B_{60}	0.2	0.1	b_6^o	+4	+0.004
B_{43}	1.2	0.6	b_4^3	+27	+0.03
C_{43}	0.7	0.6	c_4^3	+2	+0.001
B_{63}	-0.1	0.1	b_6^3	-170	0.2
C_{63}	0.1	0.1	c_6^3	+124	0.1
B_{66}	-0.06	0.08	b_6^6	-9	-0.009
C_{66}	-0.05	0.16	c_6^6	-9	-0.008

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° but centred around 55° 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° 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° 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° periodicity is noted. However, by the time $\theta = 70^{\circ}$ is reached the 60° periodicity disappears and is replaced by a 180° periodicity. A 180° 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° and 91° apart, the discrepancy from 90° 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}.

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.

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```
      C                                                                
      C                                                                
      C                 12 PARAMETERS = GX,GY,GZ,...                    
      C                    A3,D43,D66,D76                               
      C                                                                
      C              (1)  READS IN DATA,PERFORMS INITIAL CALCULATIONS & CALLS
      C  SUBPROGRAMS CALLED                                            
      C              DTQL - SUBRLTIN                                    
      C              SIN  - SINE OF REAL ANGLE IN RADIANS              
      C              COS  - COSINE OF REAL ANGLE IN RADIANS            

      1          IMPLICIT REAL*8(A-H,O-Z)                             
      2          COMPLEX*16 A,B,H,BH,DCONJG,TWIC                      
      3          COMMON A(36),B(36),H(36),DH(36,12),D15(12),D25(144),D35PDB(9),
             1 D42PDB(9),D14PDB(9),D5APDB(9),CO1D1(7),CO4PD(5),CO4PD7(4),DH25(2),
             2 THETA(16),PHI(16),HDP(16),HB(112),P(12),GND,OFF,PI,IT,ITM
      4          DIMENSION HEADER(10),CNAME(10)                       
      5          DATA TWIC/(0.D0,1.D0)/                               
      C  FORMAT STATEMENTS  INPUT 100-106    OUTPUT 120-126           
      6       99 FORMAT(2I5)                                          
      7      100 FORMAT(I5,F5.1,I5/(10A8))                            
      8      101 FORMAT(16F5.1)                                       
      9      102 FORMAT(8F10.2)                                       
     10      103 FORMAT(7F10.5)                                       
     11      104 FORMAT(5F10.6)                                       
     12      105 FORMAT(4(6F10.6/),7F10.6/,2(5F10.6/),2F10.6)         
     13      106 FORMAT(8F10.6)                                       
     14      119 FORMAT(1H1,10X,'NUMBER OF ORIENTATIONS =',I5,5X,     
             1 'NUMBER OF ITERATIONS =',I5)                           
     15      120 FORMAT(//5X,'SIZE OF MATRIX =',I5,5X,'SPIN VALUE =',F5.1,5X,
             1 'NUMBER OF PARAMETERS =',I5,(//10A8))                  
     16      121 FORMAT(//12(F8.1,2X))                                
     17      122 FORMAT(//12F10.5)                                    
     18      123 FORMAT(//5X,'POLEFACE CORRECTION =',F10.6,5X,'INTERCEPT =',F10.6,
             1 'PROTON MHZ TO GAUSS =',F10.6,5X,'OPPH G VALUE =',F10.6,5X,
             2 'FREE ELECTRON G VALUE =',F10.6)                       
     19      124 FORMAT(1H1,4X,'GX',8X,'GY',8X,'GZ',8X,'D20',7X,'A43',7X,...
             1 'D43',7X,'C43',7X,'B63',7X,'C63',7X,'B66',7X,'C66')    
     20      125 FORMAT(//12F10.6)                                    
     21      126 FORMAT(//20X,'ITERATION =',I5)                       
     22      229 FORMAT(20X,'SMALL B PARAMETERS.  UNITS KGAUSS')      
     23      230 FORMAT(20X,'GX =',F12.7,10X,'GY =',F12.7,10X,'GZ =',F12.7/,
             1 20X,'D20=',G14.6,8X,'A40=',G14.6,8X,'B60=',G14.6)      
     24      231 FORMAT(/20X,'B43=',G14.6,8X,'C43=',G14.6,8X,'B66=',G14.6)
     25      232 FORMAT(/20X,'C43=',G14.6,8X,'C63=',G14.6,8X,'C64=',G14.6)
     26      233 FORMAT(20X,'SMALL D PARAMETERS.  UNITS *9-04 CM-1')   
      C                                                                
      C          READ INPUT DATA CARDS                                 
     27          READ 99,LM,ITM                                        
     28          READ 100,N,SPIN,IMAX,CNAME,HEADER                     
     29          PRINT 119,LM,ITM                                      
     30          PRINT 120,N,SPIN,IMAX,CNAME,HEADER                    
     31          READ 101,(THETA(L),L=1,LM)                            
     32          READ 101,(PHI(L),L=1,LM)                              
     33          READ 102,(HDP(L),L=1,LM)                              
     34          PRINT 122,(HDP(L),L=1,LM)                             
     35          NH=LM*7                                               
     36          READ 103,(HB(INDEX),INDEX=1,NH)                       
     37          READ 104,ACI,CAPI,PMHC,GPP,OFF                        
```

```
          READ 105,CADIMC,PHIMC,PMHC,ADJ,CADJ,TTM,LM,NB

C     READ INITIAL VALUES OF PARAMETERS
C
          READ 104,(P(I),I=1,IMAX)
C
C              CORRECT AND CONVERT FIELD VALUES.
C
          AP=ADJ*P*MC
          CAP=CADJ*PHIP
          DO 150 L=1,LM
          HDP(L)=HDP(L)*AP
          LIND=L*7
          LIM=LIND-6
          DO 150 INDEX=LIM,LIND
          HB(INDEX)=HB(INDEX)*AP+CAP
150       CONTINUE
          PRINT 122,(HDP(L),L=1,LM)
          PRINT 121,(THETA(L),L=1,LM)
          PRINT 121,(PHI(L),L=1,LM)
          DO 143 J=1,7
143       PRINT 122,(HB(INDEX),INDEX=J,NB,7)
          PRINT 123,ADJ,CADJ,PMHC,CDP,CEP
          DO 310 IT=1,ITM
          PRINT 130,IT
          PRINT 124
C
C     PRINT INITIAL PARAMETER VALUES.
C
          PRINT 125,(P(I),I=1,IMAX)
C              INITIALIZE MATRIX SET UP  A(IAB),B(IAB)
C
          DO 290 IAB=1,36
          DO 291 I=1,IMAX
291       DH(IAB,I)=0.D0
          H(IAB)=0.D0
          B(IAB)=0.D0
290       A(IAB)=0.D0
          DR2=DSQRT(2.D0)
          ID=1
          IAB=1
          IP=3
          DO 300 K=1,NB
          A(IAB)=G02P08(K)*P(4)+G04P08(K)*P(5)+G06P08(K)*P(6)
          B(IAB)=G01P08(K)*P(3)
          DH(IAB,4)=G02P08(K)
          DH(IAB,5)=G04P08(K)
          DH(IAB,6)=G06P08(K)
          IAB=IAB+IP
300       ID=ID+1
          IAB=2
          IP=3
          NY=NB-1
          DO 301 K=1,NY
          A(IAB)=-P(1)*G01P1(K)/DR2
          B(IAB)=P(2)*G01P1(K)/DR2
          IAB=IAB+IP
301       ID=ID+1
          IAB=7
```

```
        T=1
        IP=II=0
        DO 302 I=1,NZ
        A(IAB)=COARC(K)*P(7)+COARD(K)*P(8)
        B(IAB)=COARC(K)*P(8)+COARD(K)*P(10)
        DM(IAB,7)=COARC(K)
        DM(IAB,8)=+IBAC*(COARC(K))
        DM(IAB,9)=COARD(K)
        DM(IAB,10)=+IBAC*(COARD(K))
        IAB=IAB+IB
  302   II=II+1
        IAC=22
        ID=P
        NY=NM-4
          DO 304 K=1,NY
        A(IAB)=COARA(K)*P(11)
        B(IAB)=COARA(K)*P(12)
        DM(IAB,11)=COARA(K)
        DM(IAB,12)=+IBAC*(COARA(K))
        IAB=IAB+IB
  304   IB=IB+1
        CALL BTMI
  210   CONTINUE
        P(1)=P(1)*CFF
        P(2)=P(2)*CFF
        P(3)=P(3)*CFF
        P(4)=P(4)*(1.5D0**0.5D0)
        P(5)=P(5)*2.D0*(10.D0/7.D0)**0.5D0
        P(6)=P(6)*315.D0/(231.D0**0.5D0)
        FT=15.D0*(2.D0**0.5D0)
        P(7)=P(7)*FT
        P(8)=P(8)*FT
        ST=157.5D0*(5.D0*11.D0)**0.5D0
        P(9)=P(9)*ST
        P(10)=P(10)*ST
        P(11)=P(11)*157.5D0
        P(12)=P(12)*157.5D0
        PRINT 220
        PRINT 230,(P(I),I=1,6)
        PRINT 231,(P(I),I=7,11,2)
        PRINT 232,(P(I),I=8,12,2)
        DO 630 I=4,IMAX
  630   P(I)=P(I)*0.03500
        PRINT 235
        PRINT 230,(P(I),I=1,6)
        PRINT 231,(P(I),I=7,11,2)
        PRINT 232,(P(I),I=8,12,2)
        STOP
        END
```

APPENDIX B

```
                  ...........
                     ...................
                     SUBROUTINE CALLS:
                        CEIGEN - PROVIDED
                        DATAN - PROVIDED
                        COS
                        DABS
136         IMPLICIT REAL*8 (A-H,O-Z)
137         COMPLEX*16 A,P,H,PP,EVECT(64),EVECT1(8),EVECT2(8),.,...,...,
           3DUT(36,12)
138         COMMON /(34),R(36),H(36),DH(36,12),D1F(12),D2F(144),...DDUT(8),
           1DD2DDB(8),DD4BDB(8),DD6DDB(8),CD8H1(7),CD8B2(5),CD8B3(9),....(.),
           2 THETA(16),PHI(16),HDD(16),HB(112),W(12),...,...,....,...,
139         DIMENSION(16),EX(7),EY(7),DB(12),H(12),SIGMA(12),R(144),...........
140         DATA IMAG/(0.D0,1.D0)/..
141     127 FORMAT(//I5)
142     200 FORMAT(//12F10.6)
143     201 FORMAT(20X,'NEW VALUES FOR PARAMETERS')
144     202 FORMAT(20X,'MEAN SQUARE DEVIATION =',G14.6,10X,' ...MEAN SQUA.
           1DEVIATION =',G14.6)
145     203 FORMAT(20X,'STANDARD DEVIATION FOR EACH PARAMETER')
146     204 FORMAT(20X,'DEVIATION =',G10.3)
147     205 FORMAT (10X,'VALUE OF',I2,'TH PARAMETER IS NOT CONVERGENT.')
148     210 FORMAT('0',2G8.1,/4G8.1,/6G8.1,/8G8.1,/10G8.1,/12G8.1,/3G8.1,
           1 /14G8.1,/90X,2G8.1)
149     220 FORMAT(//12G10.3)
150     225 FORMAT('0',5X,6G15.7)
C
C                   CALCULATE ENERGY DIFFERENCE FROM EXPERIMENTAL FREQUENCY.
C                   CALCULATE COMPONENTS OF FIELD VALUES.
C
151         NN=L*(N-1)
152         IMAX2=IMAX*IMAX
153         DR2=DSQRT(2.D0)
154         DO 350 IJ=1,IMAX2
155     350 D2F(IJ)=0.D0
156         DO 351 I=1,IMAX
157     351 D1F(I)=0.D0
158         XLSF=0.D0
159         DO 540 L=1,LN
160         E(L)=HDD(L)*GDD/GEE
161         THETAR=THETA(L)*.0174533
162         PHIR=PHI(L)*.0174533
163         STHTH=DSIN(THETAR)
164         COSTH=DCOS(THETAR)
165         SINPH=DSIN(PHIR)
166         COSPH=DCOS(PHIR)
167         X=COSPH*SINTH
168         Y=SINPH*SINTH
169         Z=COSTH
170         LIND=L*(N-1)
171         LIB=LIND-N+2
172         DO 540 INDEX=LIB,LIND
173         HX=HB(INDEX)*X
174         HY=HB(INDEX)*Y
175         HZ=HB(INDEX)*Z
C
C                   SETTING UP MATRIX ELEMENTS OF H(IAB)
C
176         IAB=1
177         ND=N+1
```

```
                    ...
              ...  I=1,...
         1A=T1
   508  CALL STC (OPT(IA ,I), N(IN ,J), SVECT ,  ,I  , A   C )
         LA   M=3
         DO 508 I=7,10
         IA2=1
   508  CALL STC (OPT(I2 ,I), PN(IN ,J), SVECT, , ,IN , A  )
         L PSIZ=4
         DO 510 I=11,13
         IA =1
   510  CALL STCM(OPT(IA ,I), UN(IN ,I), SVECT, , T, LA  N )
         LA DD =2
         DO 512 I=12,14
         IA =1
   512  CALL STC (OPT(IA ,I), PN(IN ,I), SVECT, , K , LA   )
         LA  D =4
         I=1
         IA =1
   514  CALL STC (OPT(IA ,I), P (IA ,I), SVECT, , KM, L      )
         XLSP=XLSP+(DELTA**2)
C
C                  SETTING UP DE(INDEX,I)
C
         K =K +1
         KK =(K *K +K )/2
         DO 520 I=1,IMAX
         DE(I)=OPT(KK +K ,I)-OPT(KK ,I)
C
C                  SETTING UP DF/DP(I) I=1,IMAX
C
         DIF(I)=DIF(I)+(2*DELTA*DE(I))
   520  CONTINUE
C
C                  SETTING UP D2F/DP(I)DP(J)
C
         DO 540 I=1,IMAX
         DO 540 J=1,IMAX
         IJ=I+(J-1)*IMAX
         D2E=0.D0
         DO 539 ID=1, D
         IF(ID.LT.KM)GO TO 522
         IF(ID.EQ.KM) GO TO 521
         KID=KM+(ID*ID-ID)/2
         D TI=DCONJG(OPT(KID,I))
         D TJ=OPT(KID,J)
         IF(ID.EQ.DM) GO TO 533
   521  IF(ID.LT. K) GO TO 523
         KIDA=PK+(ID*ID-ID)/2
         D TIA=DCONJG(OPT(KIDA,I))
         D TJA=OPT(KIDA,J)
         GO TO 525
   522  KID=ID+(K *K -K )/2
         D TI=OPT(KID,I)
         DPTJ=DCONJG(OPT(KID,J))
         KIDA=ID+(K *K -PK)/2
         DPTIA=OPT(KIDA,I)
         D TJA=DCONJG(OPT(KIDA,J))
         GO TO 525
   523  KIDA=ID+(PK*PK- K)/2
         D TIA=OPT(KID ,I)
```

```
         ...T...=TI...A/...T(I...,.I))
  531  ...F...=2S*2...I...TJA...IJ/(6...(...)-...(..I.))
         GO TO 5..
  533  ...2...=D2F-2...0**...TI*...TJ/(...(...V)-G...(I...))
         G) TO 5.0
  535  ...2...=...2...*2.0**...TIA*...TJA/(...(...)-...(...))-2....**...TI*...TJ/
      1 (...(K...)-G...(I...))
  5..  CONTINUE
       ...2F(IJ)=...2F(IJ)+(2.00*...E(I)*...F(J))-...G...*...*...L...
  540  CONTINUE
       NF...E...=...-I...AX
       XLSF=XLSF/NF...E...
       ...7 542 I=1,I...AX
       ...1F(I)=...1F(I)/...F...E...
       DO 542 J=1,I...AX
       IJ=I+(J-1)*I...AX
       D2F(IJ)=D2F(IJ)/NF...EE
       A...2F(IJ)=D2F(IJ)
  542 CONTINUE
C
C                FIND PREDICTED DISPLACEMENTS D(I), CALCULATE ...E... VALUES
C                FOR PARAMETERS P(I), PRINT RESULTS TOGETHER WITH
C                MEAN SQUARE DEVIATION FOR FITTING AND STANDARD DEVIATION
C                FOR EACH OF THE PARAMETERS
C
       CALL D...INV(D2F,I...AX,DETER)
       DO 550 I=1,I...AX
       IJ=I-I...AX
       D(I)=0.D0
       DO 550 J=1,I...AX
       IJ=IJ+I...AX
  550 D(I)=D(I)-D2F(IJ)*D1F(J)
       PRINT 200,(D(I),I=1,I...AX)
       DO560 I=1,I...AX
  560 P(I)=P(I)+D(I)
       PRINT 201
       PRINT 225,(P(I),I=1,I...AX)
       XLSNEW=XLSF
       II=-I...AX
       DO600 I=1,I...AX
       II=II+I...AX+1
       XLSNEW=XLSNEW+D1F(I)*D(I)+(A...2F(II)*D(I)*D(I))/2....
       J...IN=I+1
       IF(I.GE.I...AX) GO TO 600
       DO 590 J=J...IN,I...AX
       IJ=II-I+J
       XLSNEW=XLSNEW+A...2F(IJ)*D(I)*D(J)
  590 CONTINUE
  600 CONTINUE
       II=-I...AX
       IF(D2F(II).LT.0.D0) PRINT 205,I
       DO 620 I=1,I...AX
       II=II+I...AX+1
  620 SIGMA(I)=DSQRT(DABS(D2F(II)*XLS...F*2.D0/NF...EE))
       PRINT 202,XLSF,XLSNEW
       PRINT 203
       PRINT 200,(SIGMA(I),I=1,I...AX)
       RETURN
       END
...***  FORMAT STATEMENT    127 IS UNREFERENCED
...***  FORMAT STATEMENT    210 IS UNREFERENCED
```

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 $I \leqslant J$.   For $I \geqslant J$ 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:

                        O compute eigenvalues and eigenvectors
                        I compute eigenvalues only. (R need not
                        be dimensioned but must still appear in
                        calling sequence.)

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-CM, 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.

```
             SUBROUTINE CEIGN(CA,CR,N,MV)
C
C     COMPUTES DOUBLE PRECISION EIGENVALUES AND EIGENVECTORS  (MTLESS MV )
C     OF THE HERMITEAN MATRIX  CA  OF DIMENSION N .
C     THE JACOBI METHOD IS USED.
C     EIGENVALUES ARE STORED IN THE DIAGONAL ELEMENTS OF  CA  IN ASCENDING
C     ORDER. THE EIGENVECTORS ARE STORED COLUMNWISE IN  CR  IN THE SAME
C     SEQUENCE.
C     W. E. BAYLIS.   FEB 1972.
C
466          IMPLICIT REAL*8 (A,D,G,O-Z), COMPLEX*16(C)
467          COMPLEX*16 ONE/(1.0D0,0.0D0)/,ZERO/(0.0D0,0.0D0)/,DCONJG
468          REAL*8 COSP,COSP2,CDABS
469          DIMENSION CA(36),CR(64),CSINP(2)
C
C     CHECK DIMENSION
C
470          IF(N-1)1,2,5
471        1 PRINT 200,N
472      200 FORMAT(' ERROR. ATTEMPT TO DIMENSION CEIGEN BY N ',I6,'.'/' STOP
            .XECUTION.')
473          STOP
474        2 IF(MV .EQ. 1) GO TO 4
475          CR(1) = ONE
476        4 RETURN
C
C     GENERATE IDENTITY MATRIX
C
477        5 RANGE = 1.0D-12
478          IF(MV .EQ. 1) GO TO 25
479          IQ = -N
480          DO 20 J=1,N
481          IQ = IQ + N
482          DO 20  I=1,N
483          IJ = IQ + I
484          CR(IJ) = ZERO
485          IF(I .EQ. J) CR(IJ) = ONE
486       20 CONTINUE
C
C     COMPUTE INITIAL AND FINAL NORMS
C
487       25 ANORM = 0.0D0
488          Y = 0.0D0
489          IJ = 0
490          DO 35 J=1,N
491          DO 35 I=1,J
492          IJ = IJ + 1
493          X = CA(IJ)*DCONJG(CA(IJ))
494          ANORM = ANORM + X
495          IF(I .EQ. J) GO TO 35
496          Y = Y + X
497       35 CONTINUE
498          ANORM = 1.41400*DSQRT(ANORM)
499          ANRMX = ANORM*RANGE/DFLOAT(N)
500          IF(Y .LE. ANRMX) GO TO 165
C
C     INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THR
C
501          IND = 0
502          THR = ANORM
503       45 THR = THR/DFLOAT(N)
```

```
              L=L+1
585           Y = (L*L-1)/2
587           LL = L? + 1
588           I?? = ?*(L-1)
589    ??? I? = (??-1)/?
590           I? = L + ??

C
C     COMPUTE ELEMENTS OF ?X? ROTATION MATRIX IF ????????????? ???
C     LARGER THAN ???
C
511           GAP = C?ABS(CA(L?))
512           IF(GA? .LT. T??) GO TO 130
513           ?? = ?D + ?
514           I?? = ??(?-1)
515           I?? = ?
516           Y = CA(L?)
517           IF(Y .LT. 0.0D0) GA? = -GA?
518           X = (CA(LL) - CA(??))/2.0D0
519           Y = GA?/DSQRT(Y*Y+GA?*GA?)
520           IF(X .LT. 0.0D0) Y = -Y
521           STNP = Y/DSQRT(2.D0*(1.0D0 + DSQRT(1.0D0 - Y*Y)))
522           STNP2 = STNP*STNP
523           COSP2 = 1.0D0 - STNP2
524           C?SP = DSQRT(COSP2)
525           CSTNP(1) = GA?*STNP/CA(L?)
526           CSTNP(2) = DCONJG(CSTNP(1))
527           CSTN2P = 2.0D0*GA?*STNP*COSP?
C
C     ?STATE COLUMNS AND ROWS ? AND K?
C
528           ID = ?
529           DO 125 I=1,?
530           ID = ID + I - 1
531           IF(I-?) 85,115,90
532    85    IH = I + ?D
533           KCO?J = 1
534           IF(I-L) 100,115,105
535    100   IL = I + LD
536           LCO?J = 1
537           GO TO 110
538    90    IH = M + ID
539           KCO?J = 2
540    105   IL = L + ID
541           LCO?J = 2
542    110   CX = CA(I?)*CSTNP(KCO?J)
543           CY = CA(IL)*CSTNP(3-LCO?J)
544           IF(KCO?J .NE. LCO?J) GO TO 112
545           CA(IL) = CA(IL)*COSP + DCONJG(CX)
546           CA(I?) = CA(I?)*COSP - DCONJG(CY)
547           GO TO 115
548    112   CA(IL) = CA(IL)*COSP + CY
549           CA(I?) = CA(I?)*COSP - CX
550    115   IF(?-V .NE. 1) GO TO 125
551           I?P = IL? + ?
552           I?? = I?? + ?
553           CY = CP(IL?)*COSP + CP(I?P)*CSTNP(1)
554           CP(I?P) = CP(I?P)*COSP - CP(IL?)*CSTNP(2)
555           CP(IL?) = CY
556    125   CONTINUE
557           Y = CA(IL)*STNP2 + C?(I??)*COSP? - ??? *??
```

```
              IF(I .LE. K) ... IF ...
       CA( ) =
       CA(LI) = 2.

140   IF(I .LE. K) GO TO 140
      I = -K
      GO TO 60
150   IF(L .EQ. K-1) GO TO 150
      L = LO
      GO TO 50
160   IF(JD .NE. K) GO TO 160
      ISS = 0
      GO TO 50
160   IF(IS .GT. SMAX) GO TO 40
```

C   SORT EIGENVALUES AND EIGENVECTORS
C

```
160   IO = -N
      LL=0
      DO 165   I = 1,N
      IO = IO + N
      LL = LL + I
      JC = N*(I-2)
      X = CA(LL)
      DO 165 J=I,N
      JC = JC + N
      MM = (J*J+J)/2
      Y= CA(MM)
      IF(X .LE. Y) GO TO 165
      CA(LL) = Y
      CA(MM) = X
      X = Y
      IF(MV .EQ. 1) GO TO 165
      DO 160  K=1,N
      ILR = IO + K
      IMR = JC + K
      CX = CR(ILR)
      CR(ILR) = CR(IMR)
160   CR(IMR) = CX
165   CONTINUE
      RETURN
      END
```

```
A36         COMPLEX AP(378),A(36),T(64),ZERO,DCONJG
A37         DATA ZERO/(0.D0,0.D0)/
A38         DO 5 I,I=1,36
A39     5   AP(I,I)=ZERO
A40         LAMBDA=LAMBDA+1
A41         M=2*N+1
A42         DO 20 I=KK,M
A43         DO 15 J=1,N
A44         IJ=I+(J*J-J)/2
A45         IF(I.GT.J) IJ=J+(I*I-I)/2
A46         AP(IJ)=ZERO
A47         DO 10 K=LAMBDA+1,N
A48         L=K-LAMBDA
A49         LK=L+(K*K-K)/2
A50         LI=L+(I-1)*N
A51         KJ=K+(J-1)*N
A52         KI=LI+K-L
A53         LJ=KJ+L-K
A44    10   AP(IJ)=DCONJG(T(LI))*A(LK)*T(KJ)+T(LJ)*DCONJG(A(LK))*T(KI)+
A45         IF(I.GT.J) AP(IJ)=DCONJG(AP(IJ))
A46         IF(LAMBDA.EQ.0) AP(IJ)=AP(IJ)/2.D0
A47    15   CONTINUE
A48    20   CONTINUE
A49         DO 30 J=1,N
A50         I=J
A51         IJ=I+(J*J-J)/2
A52         AP(IJ)=ZERO
A53         DO 25 K=LAMBDA+1,N
A54         L=K-LAMBDA
A55         LK=L+(K*K-K)/2
A56         LI=L+(I-1)*N
A57         KJ=K+(J-1)*N
A58         KI=LI+K-L
A59         LJ=KJ+L-K
A60    25   AP(IJ)=DCONJG(T(LI))*A(LK)*T(KJ)+T(LJ)*DCONJG(A(LK))*T(KI)+
A61         IF(LAMBDA.EQ.0) AP(IJ)=AP(IJ)/2.D0
A62    30   CONTINUE
A63         RETURN
A64         END
```

```
332               SUBROUTINE MINV(A,N,D,L,M)
      C
      C         INVERTS A SINGLE PRECISION MATRIX ...
      C         ... D, DETERMINANT ...
      C         METHOD IS STANDARD GAUSS-JORDAN ELIMINATION ...
      C
333               IMPLICIT REAL*8(A-H,O-Z)
334               DOUBLE PRECISION A,D,BIGA,HOLD
335               DIMENSION A(225),L(15),M(15)
      C
      C         SEARCH FOR LARGEST ELEMENT
      C
336               D = 1.0D0
337               NK = -N
338               DO 80 K=1,N
339               NK = NK + N
340               L(K) = K
341               M(K) = K
342               KK= NK + K
343               BIGA = A(KK)
344               DO 20 J=K,N
345               IZ = N*(J-1)
346               DO 20 I=K,N
347               IJ = IZ + I
348            10 IF(DABS(BIGA) -DABS(A(IJ))) 15,20,20
349            15 BIGA = A(IJ)
350               L(K) = I
351               M(K) = J
352            20 CONTINUE
      C
      C         INTERCHANGE ROWS
      C
353               J = L(K)
354               IF(J-K) 35,35,25
355            25 KI = K-N
356               DO 30 I=1,N
357               KI = KI + N
358               HOLD = -A(KI)
359               JI = KI - K + J
360               A(KI) = A(JI)
361            30 A(JI) = HOLD
      C
      C         INTERCHANGE COLUMNS
      C
362            35 I=M(K)
363               IF(I-K) 45,45,38
364            38 JP = N*(I-1)
365               DO 40 J=1,N
366               JK= NK+J
367               JI = JP + J
368               HOLD = -A(JK)
369               A(JK) = A(JI)
370            40 A(JI) = HOLD
      C
      C         DIVIDE COLUMN BY MINUS PIVOT  (CONTAINED IN BIGA)
      C
371            45 IF(BIGA) 48,46,48
372            46 D=0.0D0
373               PRINT 300
374               RETURN
375            48 DO 55 I=1,N
```

```
                  A(I )  = ...
                  ...
                  A(I ) = A(I )/(  ...)
  370        55 CONTINUE
C
C                 REDUCE MATRIX
C
  300           DO 65 I=1,N
  301           IK=N*K+I
  302           HOLD = A(IK)
  303           IJ=I-N
  304           DO 65 J=1,N
  305           IJ=IJ+N
  306           IF(I-K)60,65,60
  307        60 IF(J-K) 62,65,62
  308        62 KJ=IJ+K-I
  309           A(IJ) = HOLD*A(KJ)+A(IJ)
  310        65 CONTINUE
C
C                 DIVIDE ROW BY PIVOT
C
  311           KJ=K-N
  302           DO 75 J=1,N
  303           KJ = KJ + N
  304           IF(J-K) 70,75,70
  305        70 A(KJ) = A(KJ)/BIGA
  306        75 CONTINUE
C
C                 PRODUCT OF PIVOTS
C
C
C                 REPLACE PIVOT BY RECIPROCAL
C
  307           A(KK) = 1.000/BIGA
  308        80 CONTINUE
C
C                 FINAL ROW AND COLUMN INTERCHANGE
C
  399           K = N
  400       100 K = K - 1
  401           IF(K) 150,150,105
  402       105 I=L(K)
  403           IF(I-K) 120,120,108
  404       108 JQ = N*(K-1)
  405           JR = N*(I-1)
  406           DO 110 J=1,N
  407           JK = JQ+J
  408           HOLD = A(JK)
  409           JI = JR+J
  410           A(JK) = -A(JI)
  411       110 A(JI) = HOLD
  412       120 J=M(K)
  413           IF(J-K) 100,100,125
  414       125 KI=K-N
  415           DO 130 I=1,N
  416           KI=KI+N
  417           HOLD=A(KI)
  418           JI = KI - K + J
  419           A(KI) = -A(JI)
  420       130 A(JI) = HOLD
  422           GO TO 100
```

```
 1          ...
 2          IMPLICIT REAL*8(A-H,O-Z)
 3          DIMENSION B(144),W(144),P(144)
 4          IR=0.D0
 5          IK=-N
 6          DO 10 K=1,L
 7          IK=IK+N
 8          DO 10 J=1,N
 9          IR=IR+1
10          JT=J-N
11          JS=IK
12          P(IR)=0.D0
13          DO 10 I=1,N
14          JT=JT+N
15          JS=JS+1
16       10 P(IR)=P(IR)+A(JT)*B(JS)
17          RETURN
18          END
```

APPENDIX G

Nominal Field in KG	Pole Face MHz	Centre MHz	Difference MHz
4.5	19.4761	19.4754	0.0007
6.0	25.9100	25.9087	0.0013
7.0	30.1988	30.1975	0.0013
8.0	34.4924	34.4913	0.0011
9.0	38.7812	34.7792	0.0020
10.0	43.0726	43.0707	0.0019
11.0	47.3530	47.3503	0.0027
12.0	51.6332	51.6308	0.0024

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.