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A study of the E.P.R. spectrum of potassium sulfate : copper(2+).

David John. Unwin
University of Windsor

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A STUDY OF THE E.P.R. SPECTRUM

OF K_2SO_4 : Cu^{2+}

by

(C) David John Unwin

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

1982

ABSTRACT

The system $K_2SO_4:Cu^{2+}$ produces four sets of spectra and the previously uninvestigated weak set was studied by electron paramagnetic resonance methods.

The data were fitted to the spin Hamiltonian

$$H = S.g.H + S.A.I. + I.Q.I$$

using an exact diagonalization process and a multi·dimensional least squares method. The parameters were found to be (in crystallographic co-ordinates)

gxx	gyy	gzz
2.5396+.0001	2.1296+ .0001	2.0920+.0001
gxy	gzx	gzy
0.1023+.0001	0.0347+.0001	0.0516+.0002
Axx·$10^{-4}cm^{-1}$	Ayy	Azz
205.3+0.9	19.9+ 5.6	38.5+4.0
Axy	Azx	Azy
88.3+2.0	2.3+1.6	-36.9+4.5
Qx·$10^{-4}cm^{-1}$	Qy	
20.6+2	3.8+0.6	

Diagonalization of g and A tensors show that they are highly non-coincident. This is due to a very low symmetry environment of the paramagnetic impurity. Reasonable agreement with a previously suggested charge compensation moαe   was also found.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION AND PURPOSE OF EXPERIMENT

Although the initial objective had been to study $LiK_2SO_4:Cu^{2+}$, obtaining samples proved to be difficult and $K_2SO_4:Cu^{2+}$ was investigated instead.

The course of searching for a crystal of LiK_2SO_4 with sufficient copper doping to produce strong electron paramagnetic resonance signals yielded crystals of K_2SO_4 with extremely strong signals.

Although the spectrum of $K_2SO_4:Cu^{2+}$ had previously been investigated by Abdulsabirov[1] and Freeman[2], these investigations left open the questions of non coincident g and A tensor and although Abdulsabirov[1] had evaluated three sets of spectra, the charge compensation mechanism they suggested left open the possibility of a fourth mechanism and a set of weak lines had not been investigated by 1 or 2.

The purpose of the investigation was to evaluate the spectrum of this weak set and to check agreement with both the charge compensation mechanism suggested by 1 and the non-coincidences reported by 2. For this purpose crystals containing a single isotope Cu^{63} were prepared thus yielding a greater resolution since the relaxation times (spin-lattice) at $77^{\circ}K$ were such that the Cu^{63} and Cu^{65} lines overlapped.

1

CHAPTER II

THE CRYSTAL STRUCTURE OF K_2SO_4

X-ray studies [3] have shown that K_2SO_4 is orthorhombic with $a=7.456Å$, $b=10.08Å$, $c=5.776Å$ and has space group Pnam (D_{2h}^{16}).

Each unit cell contains 4 formula units and the SO_4 groups form groups of symmetry related tetrahedra.

A diagram of the crystal structure is shown in fig. II.1 with a box around the unit cell.

The crystals were grown from aqueous solution by slow evaporation at room temperature and doped with Cu^{63} during growth.
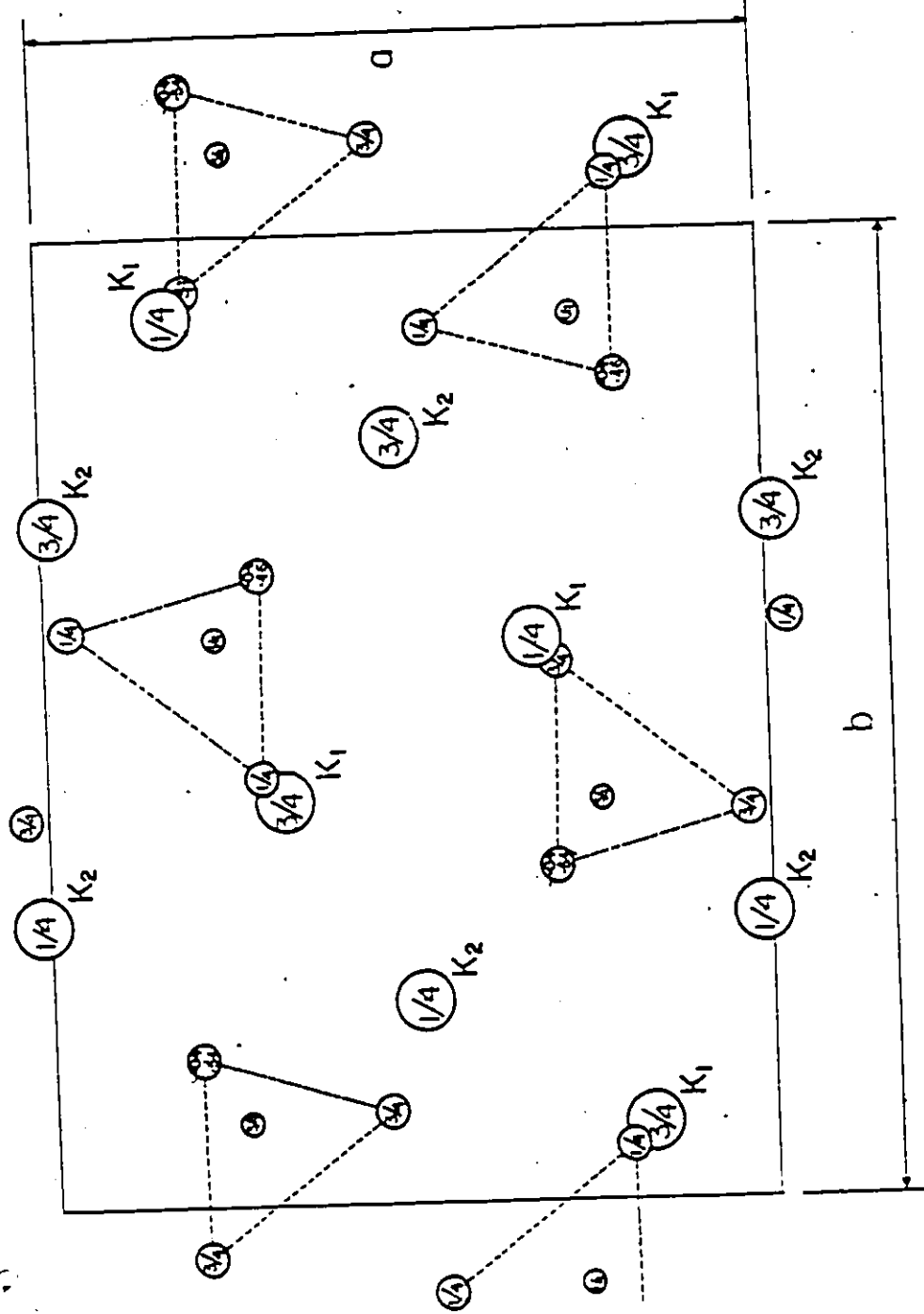
FIG II.I

CHAPTER III

THEORY

A. Electron Paramagnetic Resonance

This phenomenon was first reported by Zavoyskiy[4] in 1945
and refers to the magnetic resonance of permanent magnetic dipole
moments of electrons.

Paramagnetic centres may be produced in various ways, some
of which are,

1.) Radicals in solids

2.) Radiation damage centres

3.) Molecule-like complexes in a solid matrix

4.) Paramagnetic impurities

In our case, 4), the paramagnetic impurity is a copper dopant
Cu^{2+}.

If we consider the case of a single paramagnetic ion which
is not interacting with other impurity ions via dipole-dipole
interactions and has a single unpaired electron in an S state
with a "spin-only" magnetic dipole moment of $m_s g_s \beta$ (m_s=1/2,
β is the Bohr magneton, g_s = g free electron), then in a magnetic
field the spin degeneracy is resolved and the dipole may orient
itself parallel or antiparallel to the external magnetic field
with corresponding energies $\pm \frac{1}{2} \beta g_s H$, and this is the familiar
Zeeman effect.

Considering an ensemble of such ions we may observe magnetic dipole transitions induced between these two levels by applying a high frequency magnetic field polarized perpendicularly to H which satisfies the resonance condition.

$$h\nu = g_s \beta H$$

Resonance absorption will then be observed corresponding to dipoles being shipped from parallel to to antiparellel to $\vec{H}$.

Emission will also be induced although when the system remains in thermal equilibrium the population of $\vec{\mu}$ dipole parallel to H will exceed that of $\vec{\mu}$ dipole antiparallel to H, and a net absorption will occur.

Zeeman separations at 10KG are typically 0.01cm^{-1} and KT_{room} $\sim$ 200 cm^{-1} and since it is the slight difference in populations which gives rise to observable transitions the absorption is enhanced at lower temperatures. Another advantage of lower temperatures is that a major source of E.P.R. line broadening is spin-lattice relaxation and since spin-lattice relaxation time generally increases at lower temperatures the line width is reduced.

Other effects which cause line broadening are spin-spin interactions and exchange effects, neither of which are important in our case.

The spectra discussed here were all recorded at liquid nitrogen temperature (77° K).

Consider an ion having an orbitally non degenerate ground state with spin S. The "spin-only" interaction with an external magnetic field will be

$$= 2\beta \vec{H} \cdot \vec{S}$$

If $\vec{H}$ is parallel to $\hat{z}$ then the term splits into $(2S+1)$ equally spaced levels with energies $2\beta H M_S$ and a separation $2\beta H$ between adjacent levels.

Magnetic dipole transitions will have intensities proportional to

$$P_\epsilon = |\langle \phi_{Final} | (L_\epsilon + g_S S_\epsilon) | \phi_{Initial} \rangle|^2$$

as a consequence of Fermi's Golden Rule. The subscript ϵ denotes the component along the direction of the magnetic vector of the incident radiation. With P_ϵ as above we have, $(\vec{H} = \vec{H}z)$

$$P_x = P_y = S(S+1) - M_S(M_S+1)$$

for the transition $|SM_S\rangle \rightarrow |SM_{S+1}\rangle$ and $P_x = P_y = P_z = 0$ for all other transitions. So we have the selection rule $\Delta M_S = \pm 1$. In practice this simple scheme is complicated by crystal field effects, spin-orbit coupling and hyperfine interactions. Hyperfine interaction between the electron and the magnetic moment of the nucleus results in a further splitting of each M_S level into $(2I+1)$ levels.

B. The divalent Copper Ion

The ground state of the copper atom has the electronic configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s$$
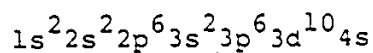
Thus giving a ^2S term, the divalent copper ion has a configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$$
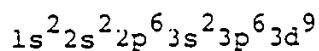
Resulting in a ^{2}D term, L=2, s=1/2. This can conveniently be treated as a hole in a closed 3d shell in the complementary scheme.

C. The Complete Hamiltonian

The complete hamiltonian operator for a paramagnetic ion a crystalline field and zero magnetic field is

$$= T + V_c + V_{so} + V_x + V_{ss} + V_{sI} + V_Q \qquad (III.1)$$

where;

$$T = \sum_k (p_k^2/2M)$$

is the total KE of the kth electron with momentum p_k and mass M and the sum extends over all the electons for the ion.

The Coulomb term V_c consists of

$$V_c = -\sum_k \frac{Ze^2}{r_k} + \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \frac{e^2}{r_{ij}}$$

The first term is the Coulomb attraction between the Kth electron and the nucleus and the second term is the Coulomb interaction between electrons summed over all electrons in the ion. The factor of 1/2 eliminates double counting.

The V_{so} term is the contribution due to spin-orbit coupling and can be written as

$$V_{so} = \sum_{ij} \lambda_{ij} \vec{l}_i \cdot \vec{s}_j$$

Where i and j are summed over all electrons in the ion. With Russell-Saunders coupling this becomes

$$\sum_i \vec{l}_i = \vec{L} \text{ and } \sum_i \vec{s}_i = \vec{S}$$

And so V_{so} becomes

$$V_{so} = \lambda \vec{L} \cdot \vec{S}$$

where   is the spin-orbit coupling constant and depends on some radial integral.

V_x represents the interaction between the paramagnetic ion and the crystal field potential

$$V_x = -\sum_k e\Phi(\vec{r}_k)$$

V_{ss} represents the magnetic dipole-dipole interaction between electrons and in our case can be set equal to zero since we are dealing with a dilute impurity with a single hole.

V_{SI} represents the magnetic interaction between unpaired electrons and the nuclear moments of both central ion and ligands. In our case no superhyperfine interaction was observed.

A full relativistic treatment of the interaction between an electron and the nuclear magnetic moment of the nucleus (see Griffith § 5.5.3) shows that the interaction adds a term

$$= 2\gamma\beta\beta_N \vec{I} \cdot \left\{ f(r^{-3}\vec{l} - r^{-3}\vec{s} + 3r^{-5}(\vec{s}\cdot\vec{r})\vec{r}) \right.$$
$$\left. + r^{-2}\frac{df}{dr}(\vec{s} - r^{-2}(\vec{s}\cdot\vec{r})\vec{r}) \right\}$$

where $f = 1 - \dfrac{E+eA_o}{2mc^2}$ and is close to unity.

After a lot of heavy algebra and with the use of the replacement theorem of equivalent operators this can be written as (within a term):

$$H_m = P\left\{ \vec{L}\cdot\vec{I} - K(\vec{S}\cdot\vec{I}) + \xi\left[L(L+1)\vec{S}\cdot\vec{I} - \frac{3}{2}(\vec{L}\cdot\vec{S})\,\vec{L}\cdot\vec{I} - \frac{3}{2}(\vec{L}\cdot\vec{I})(\vec{L}\cdot\vec{S}) \right] \right\}$$

with,

$$P = 2\gamma\beta\beta_N \langle r^{-3} \rangle$$

γ depends on the nucleus in question and β_N is the nuclear magneton,

and,

$$\xi = \frac{2 + 1 - 4S}{S(2I-1)(2I+3)(2L-1)}$$

Within a d^n configuration there should not be a Fermi contribution of the form $\vec{S}.\vec{I}$ but configuration interaction means that there is always an unpaired spin density at the nucleus from s wave contributions which are mixed in by configuration interaction. This warrants the term $\kappa(\vec{S}.\vec{I})$ but unfortunately there is no accurate way of calculating κ.

V_Q represents the quadrupole interaction between the nuclear and electronic quadrupole moments and can be written as the equivalent operator:

$$\vec{I}.Q.\vec{I}$$

Since in practice this is a small contribution, only diagonal elements are considered and application of $\vec{\nabla}.\vec{E}=\rho$ gives the extra condition that $\text{Tr}(Q) = 0$. If only $\Delta_{MI} = 0$ transitions are considered then $\text{Tr}(Q)$ is in any case indeterminate since it only adds a constant $\frac{1}{3}\text{Tr}(Q)I(I+1)$ to the Hamiltonian.

D. The spin Hamiltonian

The complete Hamiltonian as written in III.1 is too cumbersome to work with and in our case V_x is unknown.

For the fitting of the recorded spectra we make use of an equivalent Hamiltonian of the form:

$$H = \tilde{S}.g.\vec{H} + \tilde{S}.A.\vec{I} + \vec{I}.\mathcal{Q}.\vec{I}$$

The first term is the electronic Zeeman term and the g "tensor" reflects anisotropy in the spectrum due to spin-orbit and crystal field effects. The $\tilde{S}$ here is not the actual spin of the system but is an effective spin, often called "ficticious spin". $(2S+1)$ is equal to the number of electronic levels in the ground state of the ion.

The second term describes the magnetic hyperfine interaction discussed earlier. The A "tensor" describes both the magnetic interaction and the Fermi contact interaction.

The third term is an equivalent operator form for the interaction between the electronic and nuclear quadrupole moments as discussed earlier. The restriction $\text{Tr}(\mathcal{Q}) = 0$ reduces the number of empirical factors needed to fit the spectrum since $\text{Tr}(\mathcal{Q})$ only adds a constant $\frac{1}{3}\text{Tr}(\mathcal{Q})I(I+1)$ to H if $\Delta_{MI} = 0$ only transitions are considered. It's inclusion is warranted by the fact that at certain orientations $\Delta_{MI} = \pm1$ "forbidden" transitions are easily seen. This is because this non linear term in I means M_I is no longer a good quantum number.

If we choose a frame of reference which diagonalizes the g "tensor" then the Zeeman term can be written as

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

$$= (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z)$$

Similarly for the A "tensor"

$$H = (A_{x'} S_{x'} I_{x'} + A_{y'} S_{y'} I_{y'} + A_{z'} S_{z'} I_{z'})$$

Although for low symmetries it may not be possible to
diagonalize g and A simultaneously as we shall see.

CHAPTER IV

INSTRUMENTATION

A. K-Band Spectrometer

The K-band spectrometer used was of balanced bridge design, using a circulator, with the microwave frequency stabilized against the sample cavity. A block diagram is shown in fig. IV.1. The microwave power was supplied by a Varian model VA98E reflex klystron producing 30mW 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. 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 klystron in such a manner that the klystron frequency is pulled back to the frequency

12

FIG Ⅳ.I
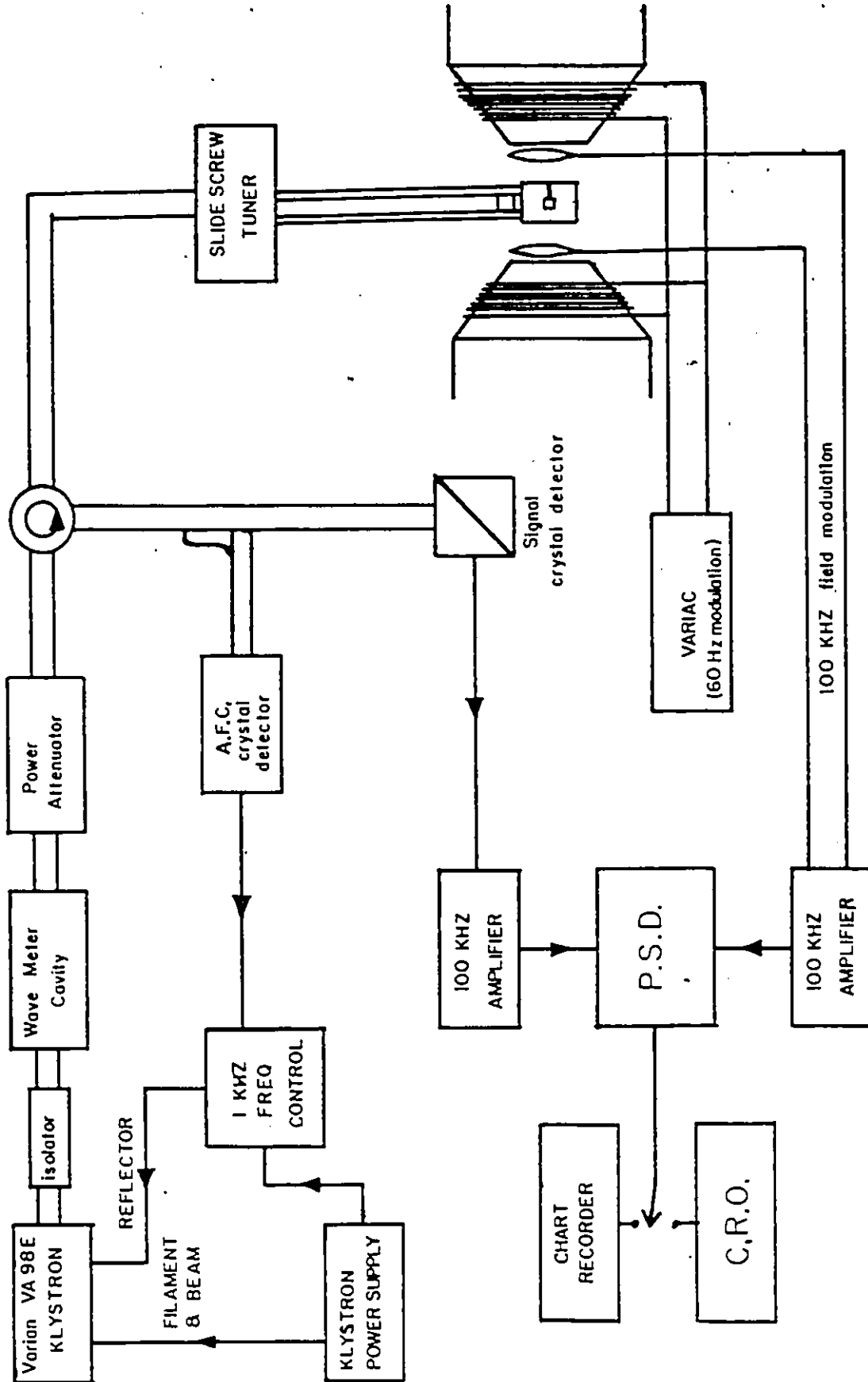
of the cavity; thus stabilizing the klystron on the resonant frequency of the cavity.

(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 another 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. Any 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.

Fig. IV.3 shows a diagram of the position of the diodes D_1 and D_2 in the detector waveguide and the transformer circuit. The lines show the distribution of E intensity and it can be seen that E_1 and E_2 are in antiphase so that the signals from

FROM RESONANT CAVITY

$\vec{E}$

D_1 $\vec{E}_1$ $\vec{E}_2$ D_2

FROM CAVITY

SIDE VIEW

FROM KLYSTRON

D_1

D_2

TO 100 KHZ AMPLIFIER
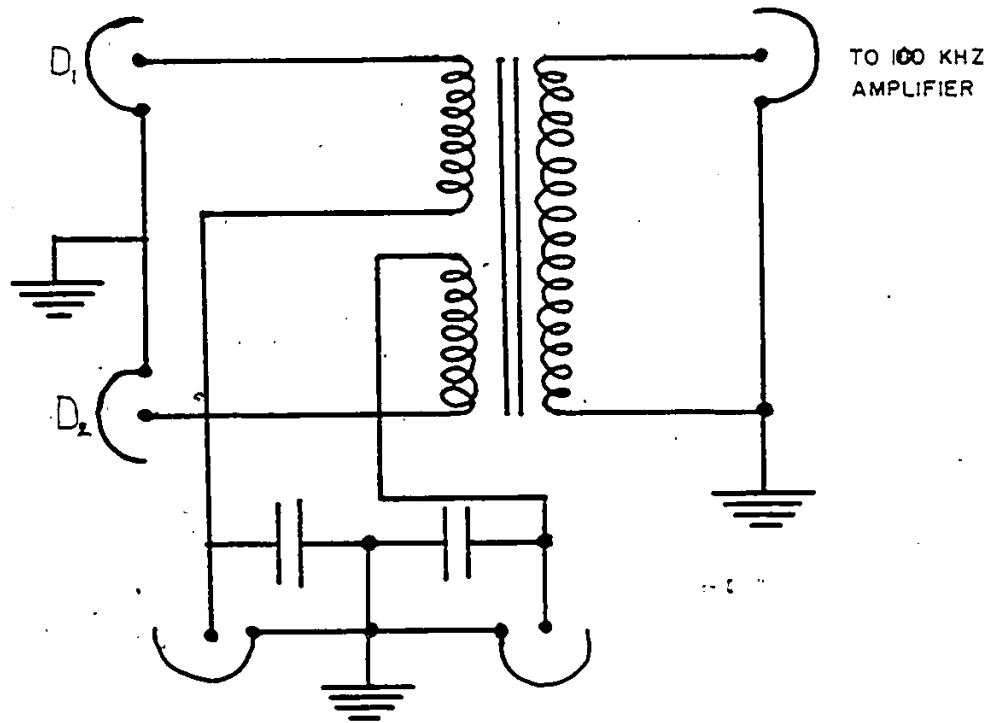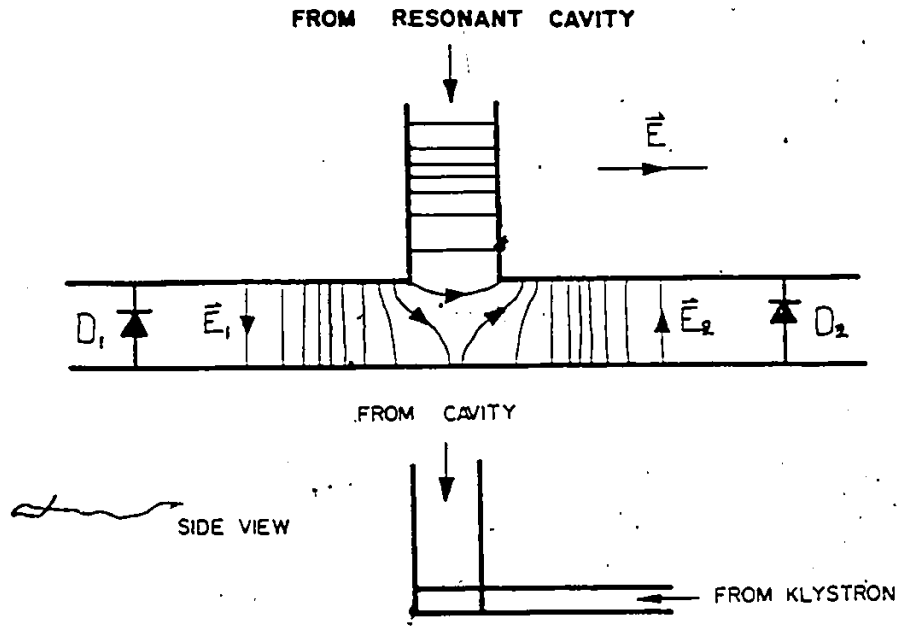
FIG IV.3

D_1 and D_2 are also in antiphase. D_1 and D_2 transmit the signal to the 100 KHz amplifier through a transformer with two oppositely directed windings and since noise at D_1 and D_2 is random it will tend to cancel half the time, thus resulting in reduced noise.

The resonant signal is preamplified and then fed into the Princeton Applied Research (P.A.R.) model J.B.-6 lock-in Amplifier, which compare the phase and frequency of the resonant signal with the original 100 KHz modulation signal in the same manner as the P.S.D. of the A.F.C. circuit. 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 facilitate display on the oscilloscope the magnetic field is modulated at 60 Hz with a "Variac", in addition to the 100 KHz modulation. 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 as both the magnetic field and crystal orientation are varied.

This provides a convenient and rapid means of studying angular variations.

The cylindrical cavity used was made of glass with an internal surface sputtered with gold. Operating in the TE011 mode the cavity has been employed successfully in this laboratory on previous occasions. In conjunction with the cavity is a rotating mechanism previously developed in this laboratory[6]. It facilitates rotation about a horizontal axis which combined with rotation of the magnet about the vertical axis allows an orbitrary orientation of magnetic field.

(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 a 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 achieve a linear sweep of up to 20 KGauss.

Magnetic field modulation at 100 KHz 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

Measurments of magnetic field strength are obtained by means of a proton magnetic resonance 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 were constructed previously in this laboratory to cover a wide frequency range and one probe proved sufficient for all measurements.

CHAPTER V

EXPERIMENTAL PROCEDURE

(i) Crystal Orientation

Because the crystals grow preferentially along the b-axis
visual examination with the aid of a binocular microscope enabled
mounting of the crystals within $\pm$ 5°. The crystals were attached
to the quartz capillaries with epoxy resin and this facilitated
placing a thermocouple (copper-constantan) in the capillary in
good thermal contact with the crystal for studies of the temper-
ature dependence of the spectra.

Using the orientation of the magnetic field about a vertical
axis and the crystal about a horizontal axis with orbitrary zero
the orientations of the magnetic field relative to the crystal
were plotted on a stereogram. The accuracy of orientation was
checked by recording spectra on a chart recorder at a point where
the spectra coincided and then recording the spectra for the
magnetic field in the reverse direction; for perfect alignment
the spectra should have been identical, in practice deviations
of less than ± 0.5° were observed. Hence the size of the error
bars in the following diagrams.

Diagrams of the spectra in the three crystallographic direc-
tions are shown in figs. IV.1-3.
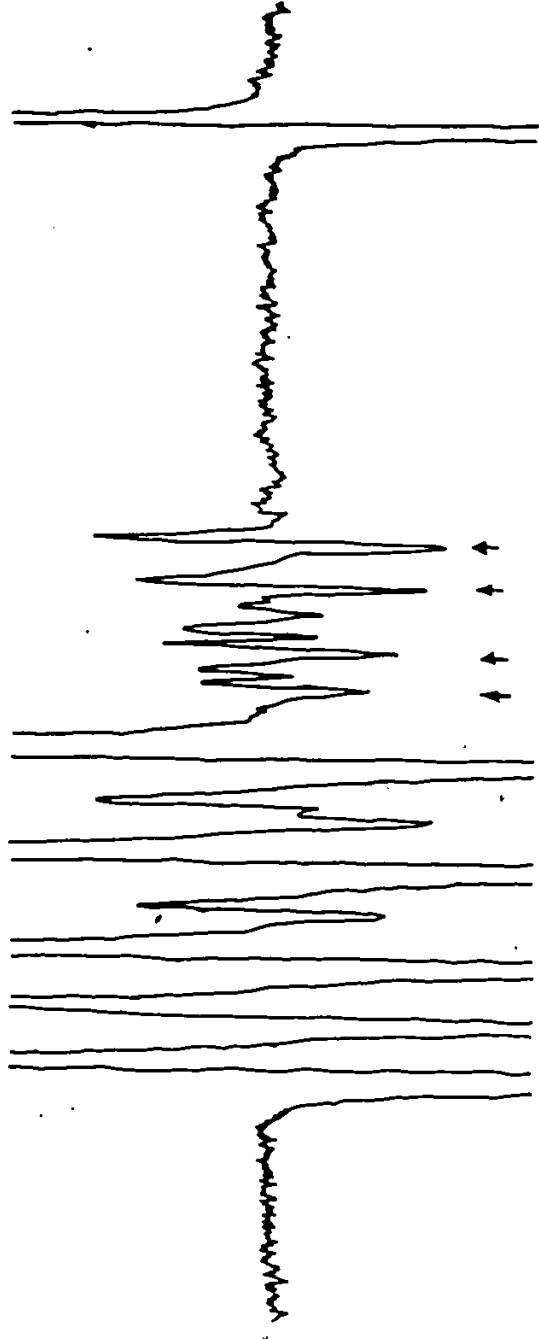
Magnetic field parallel to b

FIG $\underline{\text{IV}}$.I
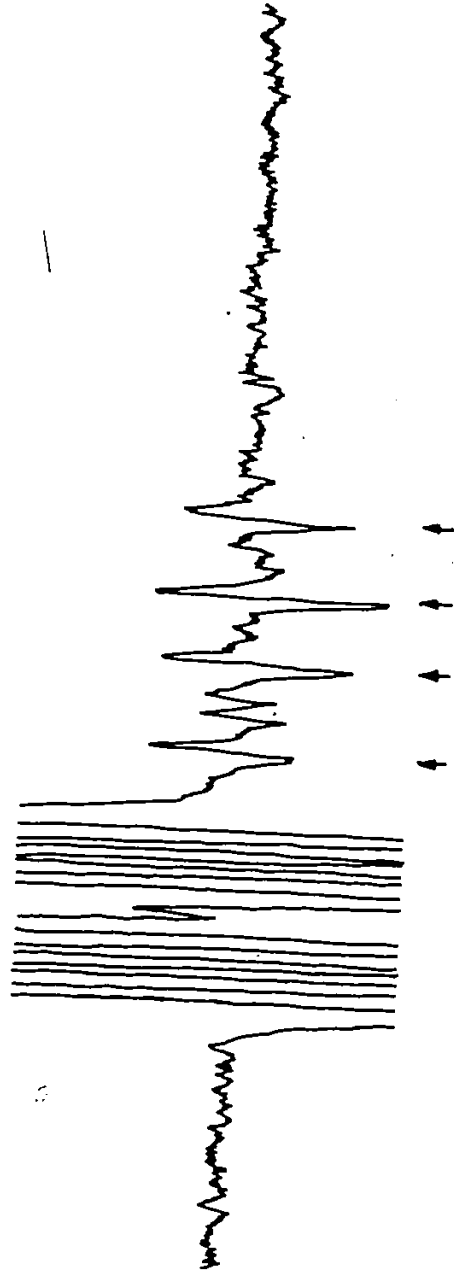
Magnetic field parallel to a

FIG IV.2

20
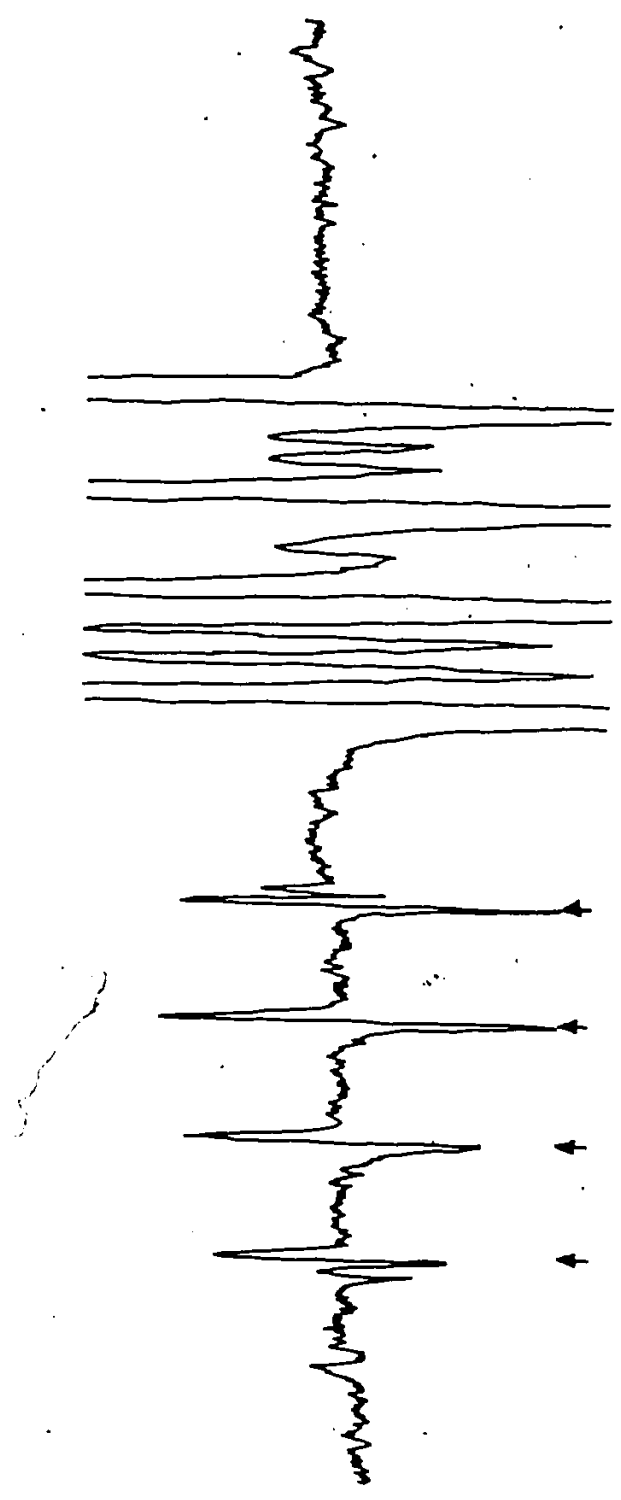
Magnetic   field   parallel   to   c

FIG Ⅳ.3

The spectra displayed three mutually orthogonal axes
coincident with the crystallographic axes at which the three
sets of strong lines coincided to form a single set of four
lines.

In the planes defined by these axes each set of four lines
splits up into two sets of four lines consistent with the unit
sell of $Z=4$ with four sets of crystallographically inequivalent
centres for an arbitrary orientation of magnetic field.

The angular variation of the set of weak lines is shown
in figs. IV 4-6 in the ab, bc, ca planes, the gaps occur where
the variation was obscured by the set of strong lines.

The orientation of the crystallographic axes was con-
firmed by x-ray analysis (see appendix 2).

Measurements were taken with a crystal doped with a single
isotope Cu^{63} and measurements of resonant fields were recorded
for 38 orientations, and the directions of magnetic field for
a right-handed system of co-ordinates were calculated directly
from a plot of all 38 orientations on a stereogram. This
allowed for convenient elimination of systematic errors and
corrections for misalignment mentioned earlier.

The measurements were taken at orientations a few degrees
apart wherever all four lines were not obscured by the stronger
ones.

For a batch of crystals grown with Cu^{63} ions, many crystals
turned out to be twinned, resulting in a complicated addition
of spectra and were of no use for this work.

BC PLANE

DPPH

RESONANT FIELD (ARB. UNITS)

ANGULAR VARIATION °

AB PLANE

DPPH

RESONANT FIELD (ARB. UNITS)

ANGULAR VARIATION °

24

CA PLANE
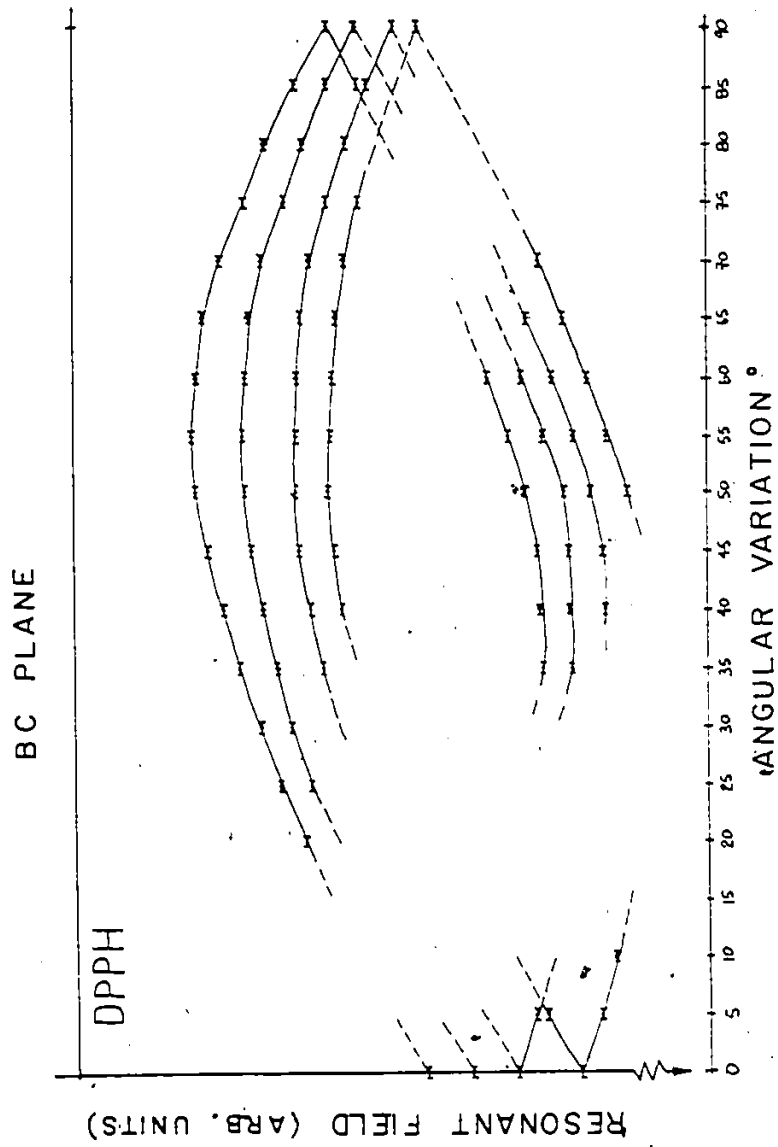
DPPH

RESONANT FIELD (ARB. UNITS)

ANGULAR VARIATION °
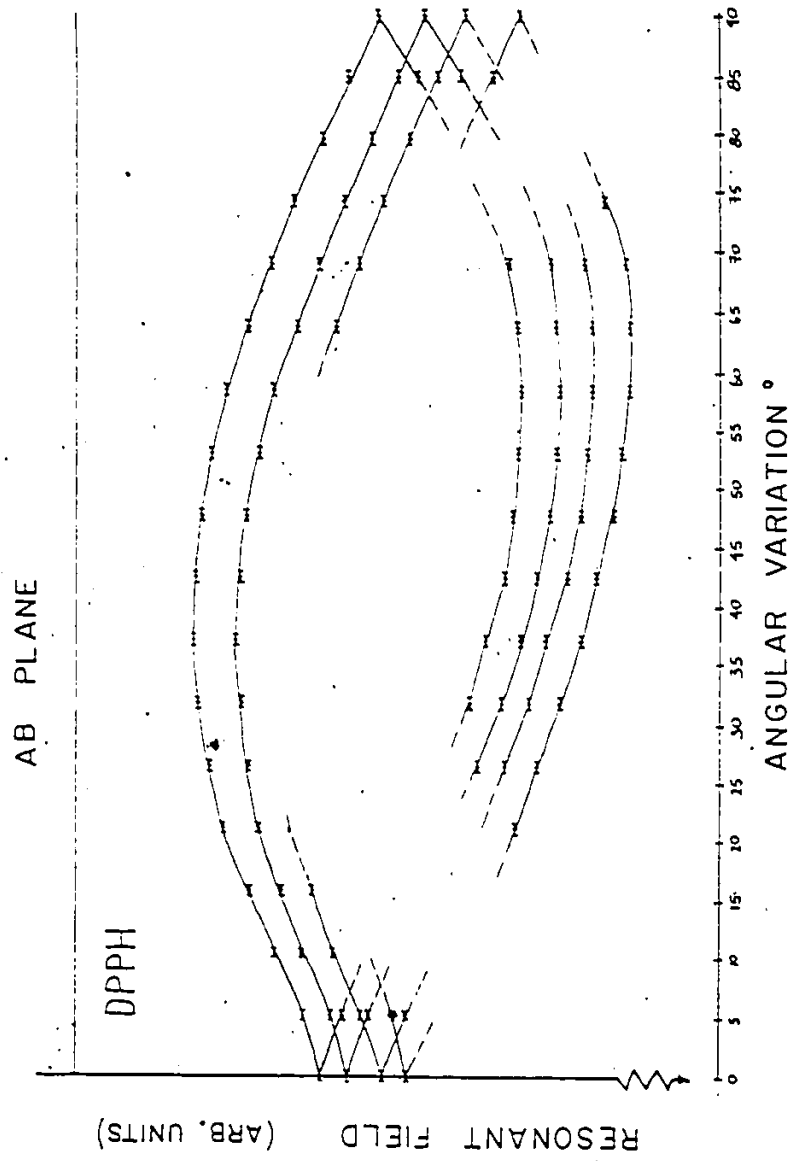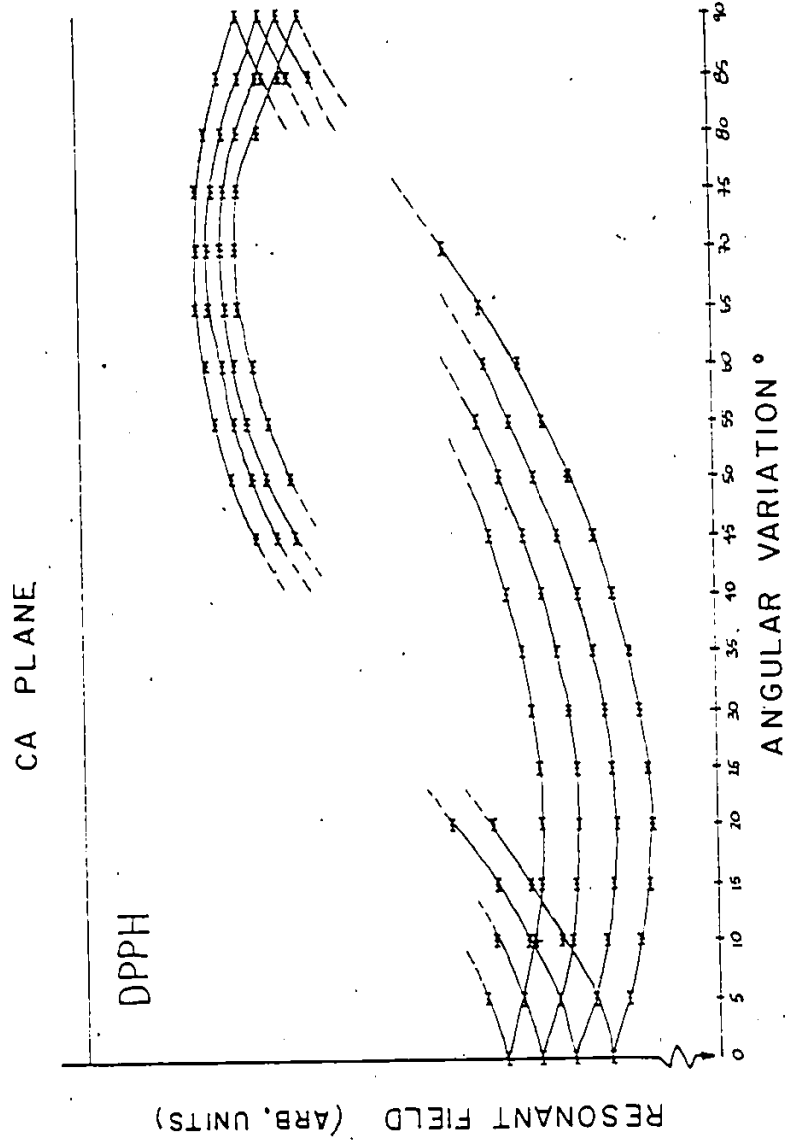
To check that the spectra were in fact due to twinning one crystal was removed from the spectrometer and carefully sliced into two and one half discarded. The spectrum resulting from half the original crystal showed a change of relative intensity of the extra lines with respect to the known set thus confirming their origin as a twinned region of crystal.

The results are tabulated in appendix 1.

(3) Measurement of Magnetic Field

A set of probes covering the frequency range 30 MHz to 53 MHz had previously been constructed in this laboratory and a single probe proved sufficient for all of our measurements.

A satisfactory signal intensity was achieved by using a grounded brass tube shielding two stiff wires which carried current to the inductor and which were separated from each other and the shielding by spacers set at intervals along the tube (see fig. V.7).

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 of the P.M.R. signal was then read from the digital output of the electronic counter. This can be converted to a magnetic field strength using the relation

$$h\nu = g_p \beta_N H$$

$$H = \frac{h}{g_p \beta_N} \cdot \nu$$

or $H(\text{KGauss}) = 0.234869 \nu(\text{MHZ})$
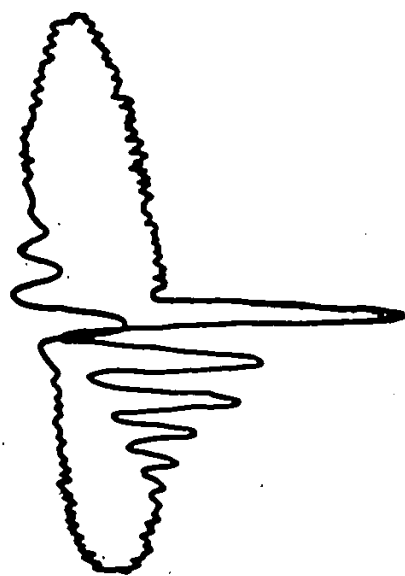
C.R.O. display of P.M.R. signal.

FIG $\underline{V}$.8

where;

H is magnetic field strength

h is Planck's constant

g_p is the proton g-value

β_N is the nuclear magneton

ν is the frequency of oscillation

Typical C.R.O. display is shown in fig V.8.

Since the 60 Hz modulation was only 20 Gauss the error in reading C.R.O. scale could not have exceeded 2 Gauss and was thus of no concern as a major source of error.

(4) Measurement of Microwave Frequency

A small amount of the free radical D.P.P.H. (diphenyl picryl hydrazyl) was attached to the sample with glycerine and acted as a marker to measure the microwave frequency using the relation

$$h\nu = g_{DPPH} \, H_{DPPH}$$

$$\nu = \frac{g_D \beta}{h} . H_D$$

where;

ν = microwave frequency

g_D = D.P.P.H. g value = 2.0036

H_D = field value at D.P.P.H. resonance.

The D.P.P.H. E.P.R. line is extremely exchange narrowed and gives a very narrow temperature independent line.

CHAPTER VI

DEVELOPMENT OF COMPUTER PROGRAM FOR FITTING OF DATA

A. The method

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[7] is obtained analytically from the following condition on the Taylor series expansion

$$f(\chi_n + h) = f(\chi_n) + h \cdot f^{l}(\chi_n) + \frac{h^2 f^{ll}}{2!}(\chi_n) + \ldots = 0$$

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

$$\frac{\partial}{\partial \chi_n} f(\chi_n + h) = \frac{\partial}{\partial \chi_n} f(\chi_n) + h \cdot \frac{\partial}{\partial \chi_n} f^{l}(\chi_n) + \ldots = 0$$

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 ($i = 1, 2 \ldots I_{max}$) l the experimentally measured magnetic field values B_l and other experimental parameters necessary such as orientation 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.

29.

where N will represent the degeneracy of the ground state. So

the Hamiltonian can be expressed as

$$H = H(P_1, P_2, \ldots P_{I_{max}}, \vec{B}, \hat{K}, T, \ldots)$$ VI.1

The Hamiltonian is represented in an n-dimensional basis

. 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.

$$\langle \alpha | H | \beta \rangle$$ VI.2

$$\langle \alpha | \partial H / \partial p_i | \beta \rangle$$ VI.3

$$\langle \alpha | \partial^2 H / \partial p_i \partial p_j | \beta \rangle$$ VI.4

The matrix elements of VI.2 and VI.3 for our Hamiltonian

are easily calculated knowing the matrix elements of $I = 3/2$

and $S = 1/2$ within the manifold of $\{ |\tilde{S}\rangle \otimes |\vec{I}\rangle \}$. As the parameters

occur linearly in the Hamiltonian with no cross products the

elements of VI.4 will be zero.

For each set of external parameters $(B, K, T, \ldots)$, (in this

case for $M(N-1)$ resonant field values), the Hamiltonian is

diagonalized using the subroutine is basically an extension of

the Jacobi method to Hermitean matrices [8,9] and is double pre-

cision, complex.

A new set of basis vectors $\{ |i\rangle \}$, (in terms of the original

set $\{ |\alpha\rangle \}$, $|i\rangle = \sum_\alpha |\alpha\rangle\langle\alpha|i\rangle$) is then obtained in which the Hamil-

tonian is diagonal

$$\langle i | H | j \rangle = E_i \delta_{ij}$$ VI.5

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 ∂_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 above the resonant lines were clearly observed.

A least squares sum is formed from:

$$f = \left\{(E_{k_1} - E_{k_2}) - \partial_k\right\}^2 \qquad \text{VI.6}$$

$$= \left\{(E_{k_1} - E_{k_2}) - \frac{g_D H_D}{gs}\right\}^2 \qquad \text{VI.7}$$

where the transition energy in VI.7 is expressed in units of Gauss and is determined from the resonant field of 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 $P = (p_1, p_2, \ldots, pi)$, representing a rector 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 :

$$\frac{\partial}{\partial P_i} f(p + \delta) \approx \frac{\partial}{\partial P_i} f(p) + \sum_j \frac{\partial^2}{\partial P_i \partial P_j} f(p) \delta_j = 0$$

the solution is:

$$\delta_i = -\sum_j M_{ij} \frac{\partial}{\partial P_j} f(p) \qquad \text{VI.8}$$

where (M_{ij}) is the inverse of $\left(\frac{\partial^2}{\partial P_i \partial P_j} f(p)\right)$

and

$$\sum_j M_{ij} \frac{\partial^2}{\partial p_j \partial p_{i'}} f(\underaccent{\tilde}{p}) = \delta_{ii'}$$

The inversion is carried out by the subroutine DMINV (see appendix 5). The value of S_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.

$$\frac{\partial f}{\partial p_i} = \frac{\partial}{\partial p_i} \frac{\sum_k \left\{ (E_{k_1} - E_{k_2}) - \frac{g_D H_D}{g_s} \right\}^2}{N_{free}}$$

$$= 2 \sum_k \left(\frac{\partial E_{k_1}}{\partial p_i} - \frac{\partial E_{k_2}}{\partial p_i} \right) \frac{\left\{ (E_{k_1} - E_{k_2}) - \frac{g_D H_D}{g_s} \right\}}{N_{free}} \qquad VI.9$$

and

$$\frac{\partial^2 f}{\partial p_i \partial p_j} = 2 \sum_k \left[\left(\frac{\partial E_{k_1}}{\partial p_i} - \frac{\partial E_{k_2}}{\partial p_i} \right) \left(\frac{\partial E_{k_1}}{\partial p_j} - \frac{\partial E_{k_2}}{\partial p_j} \right) \right.$$

$$\left. - \left(\frac{\partial^2 E_{k_1}}{\partial p_i \partial p_j} - \frac{\partial^2 E_{k_2}}{\partial p_i \partial p_j} \right) \frac{\left\{ E_{k_1} - E_{k_2} - \frac{g_D H_D}{g_s} \right\}}{N_{free}} \right] \qquad VI.10$$

where

$$\frac{\partial E_k}{\partial p_i} = \lim_{\delta_i \to 0} \left\{ \frac{E_k(\underaccent{\tilde}{p} + \delta_i \hat{\imath}) - E_k(\underaccent{\tilde}{p})}{\delta_i} \right\}$$

Where $\hat{\imath}$ is a unit rector in i - dimensional parameter space and where $E_k(\underaccent{\tilde}{p} + \delta_i \hat{\imath})$ is the eigenenergy corresponding to $E_k(\underaccent{\tilde}{p})$ of the Hamiltonian $H(\underaccent{\tilde}{p} + \delta_i \hat{\imath})$, to first order in δ_i

$$H(\underaccent{\tilde}{p} + \delta_i \hat{\imath}) \approx H(\underaccent{\tilde}{p}) + \frac{\partial H(\underaccent{\tilde}{p})}{\partial p_i} \delta_i$$

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

$$E_k(\underset{\sim}{p} + \delta_i \hat{\underset{\sim}{i}}) = E_k(\underset{\sim}{p}) + \langle K | \frac{\partial H}{\partial p_i} | K \rangle \delta_i$$

and consequently

$$\frac{\partial E_k}{\partial p_i} = \langle k | \frac{\partial H}{\partial p_i} k \rangle \qquad\qquad IV.11$$

similarly

$$\frac{\partial^2 E}{\partial p_i \partial p_j} = \lim_{\delta_i, \delta_j \to 0} \frac{E(\underset{\sim}{p} + \delta_i \hat{\underset{\sim}{i}} + \delta_j \hat{\underset{\sim}{j}}) - E(\underset{\sim}{p} + \delta_i \hat{\underset{\sim}{i}}) - E(\underset{\sim}{p} + \delta_j \hat{\underset{\sim}{j}}) + E(\underset{\sim}{p})}{\delta_i \delta_j}$$

Now to second order in δ's

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

$$+ \frac{\partial H}{\partial p_j} \delta_j + \frac{1}{2} \left(\frac{\partial^2 H}{\partial p_i^2} \delta_i^2 + \frac{\partial^2 H}{\partial p_j^2} \delta_j^2 \right)$$

$$= H(\underset{\sim}{p}) + V$$

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

$$E(\underset{\sim}{p} = \delta_i \hat{\underset{\sim}{i}} + \delta_j \hat{\underset{\sim}{j}}) = E(\underset{\sim}{p}) + \langle K | V | K \rangle + \sum_{1 \neq K} \frac{\langle K | V | 1 \rangle \langle 1 | V | K \rangle}{E_k - E_1}$$

Thus

$$\frac{\partial^2 E}{\partial p_i \partial p_j} = \langle k | \frac{\partial^2 H}{\partial p_i \partial p_j} | k \rangle + 2 \mathcal{R}e \sum_{1 \neq k} \frac{\langle k | \frac{\partial H}{\partial p_i} | 1 \rangle \langle 1 | \frac{\partial H}{\partial p_j} | k \rangle}{E_k - E_1}$$

where the matrix elements $\langle k | M | 1 \rangle$ written in terms of the old basis are

$$\langle k|M|l\rangle = \sum_{\alpha,\beta}\langle k|\alpha\rangle\langle\alpha|M|\beta\rangle\langle\beta|l\rangle \qquad\qquad VI.12$$

The similarity transformation is carried out by the sub-routine STCM (see appendix 5)

Probable errors are calculated as follows, since f may have a probable error given by $\Delta f \approx f/N_{free}$ the corresponding σ_i in pi is given by

$$\Delta f \approx \frac{1}{2}\sum_{ij} M_{ij}\,\sigma_i\sigma_j \simeq f/N_{free}$$

The values of σ_i^2 are calculated from inversion of the above giving,

$$\sigma_i^2 = 2M_{ii}^{-1}\,(f/N_{free})$$

B. The flow chart

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

1. The data is read in including all external paramenters, initial estimates of the crystal parameters and the matrix elements of operators required in the equivalent Hamiltonian. The input data after conversion is printed out.

2. The matrix elements that are independent of the field are calculated.

3. The remaining field dependent matrix elements are calculated using the components of the measured field values in addition to data utilised in 2. (see appendix 6 for RTN1)

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

Correct and convert field
values

Print Input Data

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

IT = IT + 1

Call RTN 1

Calculate parameter
Values in required units

current variables

IT   = iteration #

L   = orientation #

INDEX = Field value #

I   = Parameter #

J   = Parameter #

IAB   = Matrix element #
        (compact storage)

Initialize DIF, D2F
Calculate Experimental
ENERGY DIFFERENCE

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

CALL CEIGEN
Diagonalize Complex Matrix
H

INDEX = INDEX + 1

L=L+1

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

Transform DH to new basis

I=1+1

J=J+1

COMPUTE DE(I), DIF, D2F,D2E
Derivative Matrices in new
basis

CALL DMINV
INVERT D2F

CALCULATE Parmeter
correction D9I)
D(I) - -D2F^{-1}. DIF (I)

Calculate new value for
parameter P_i - P_i - $_i$
Standard deviation $_i$
and new mean square
deviation

Print Results

Fig. VI.1.   FLOW CHART FOR COMPUTER PROGRAMME

4. The Hamiltonian matrix form in 2 and 3 is then diagon-
    alized exactly using the subroutine CEIGEN (see appendix
    7) 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 transformation 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.12).
    This then allows calculation of DE(I), the derivative
    of the energy with respect to each parameter, see (VI.11).
    From these the first and second derivatives of the least
    squares fit are formed, D1F(I), see VI.9, and D2F(I),
    see VI.10.

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

    Steps 3 - 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 all of the
    orientations in the L = L + 1 loop.

6. As D2F involves summation of both I & J simultaneously
    as well as a summation over all of the resonant fields,
    it is not completed until the end of step 5. D2F is
    then inverted using DMINV (see appendix 7). The para-
    meter connection D(I) can then be calculated see VI.8,

the new estimate of the parameters is then determined

$$P(I) = P(I) + D(I)$$

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 $(D2F)^7$ matrices are multiplied using the subroutine DGMPRO (see appendix 8), based on IBM routine GMPROD)[10] to see that the product is the unit matrix. (see VI.8)

C. 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)^2
1	0.9190
2	0.0220
3	0.0550
4	0.0022
5	0.0200
6	0.0006

Even though the values oscillates it can be seen that convergence is quite rapid.

CHAPTER VII

DISCUSSION AND CONCLUSION

In total thirty eight orientations were used to collect
data: with orientations in all three planes included. For the
fitting of parameters in the spin Hamiltonian nineteen were
rejected because they gave for larger deviations from the trial
energy levels than the remaining twenty nine. In excess of a
dozen iterations were needed before an acceptable fit was
obtained and from then on the quality deteriorated.

The best fit parameters are tabulated in table VII.1. The
results are presented in the co-ordinate system discussed pre-
viously.

These results will be discussed in the light of previous
reports, Abdulsabirov[1] had investigated the three strong sets
of lines and had fitted data to an orthothom bic spin Hamilton-
ian,

$$H = \vec{H} \cdot \overline{\overline{g}} \cdot \vec{S} + \vec{S} \cdot \overline{\overline{A}} \cdot \vec{I}$$

in which the g and A "tensor" shared common principal axes.
They found that the orientations of these three sets axes were
completely different and correlated these orientations with the
crystallography with the help of X-ray analysis.

TABLE VII.1

g values

gxx	gyy	gzz
2.5396 ± .0001	2.1296 ± .0002	2.0920 ± .0001
gxy	gzx	gzy
0.1023 ± .0001	0.0347 ± .0001	0.0516 ± .0002

A values $(\times 10^{-4} \text{ cm}^{-1})$

Axx	Ayy	Azz
205.3 ± 0.9	19.9 ± 5.6	38.5 ± 4.0
Axy	Azx	Azy
88.3 ± 2.0	2.3 ± 1.6	-36.9 ± 4.5

Q values $(\times 10^{-4} \text{ cm}^{-1})$

Qx	Qy
20.6 ± 2.0	3.8 ± 0.6

N.B.: Above expressed in crystallographic coordinate system
described earlier.

Since Cu^{2+} is doubly charged, it substitutes for K^{1+} in the
lattic of K_2SO_4 overall electrical neutrality can only be per-
served if some kind of charge compensation occurs. Abdulsabirov[1]
proposed that this compensation occurs via a vacancy on an adja-
cent K^{1+} site. A diagram of the crystal structure of K_2SO_4 pro-
jected along the c-axis is shown in fig. VII.1. The K_1 and K_2
sites differ in environment but the four of which occur in each

unit cell are related by the symmetry of the crystal. If the Cu^{2+} impority substitutes for a K^{1+} as proposed by Abdulsabirov[1] then a vacancy on an adjacent K^{1+} site will strongly influence the g tensor and will rotate on principal axis towards the direction joining the Cu^{2+} impority and the vacancy. Abdulsabirov[1] found that the above is consistent with Cu^{2+} substituting for K^{1+} on a K_2 type site with a vacancy on an adjacent K_1 type site. They found that the principal axis of the g tensor (ie. largest principal value) for the three centre types was within a few degrees of the line joining the K_1 and K_2 type positions. These $K_2^+ - K_1^+$ directions are marked 1,2,3 on fig. VII.1. They also mention the fourth weak set of lines investigated here and suggest that they may be due to a centre produced when charge compensation occurs on the fourth adjacent K_1^+ site. The line joining K_2^+ to this fourth adjacent site drawn and labelled 4 in fig. VII.1. The directions of the principal values of the g tensor observed by Abdulsabirov[1] are inconsistent with Cu^{2+} substituting on a K_1 type site and charge compensation occuring on a K_2 type site as can easily be verified. Why substitution should occur on K_2 and not K_1 type sites is not known but it can be noted that K_1 type sites have an oxygen much closer than K_2 type sites.

Our results are in fair agreement with the above as follows. The fitted parameters in table VII.1 indicate that the g "tensor" can be adequately fitted by a symmetric tensor and the A "tensor" not so adequately although as can be seen any observed asymmetry in A is slight.
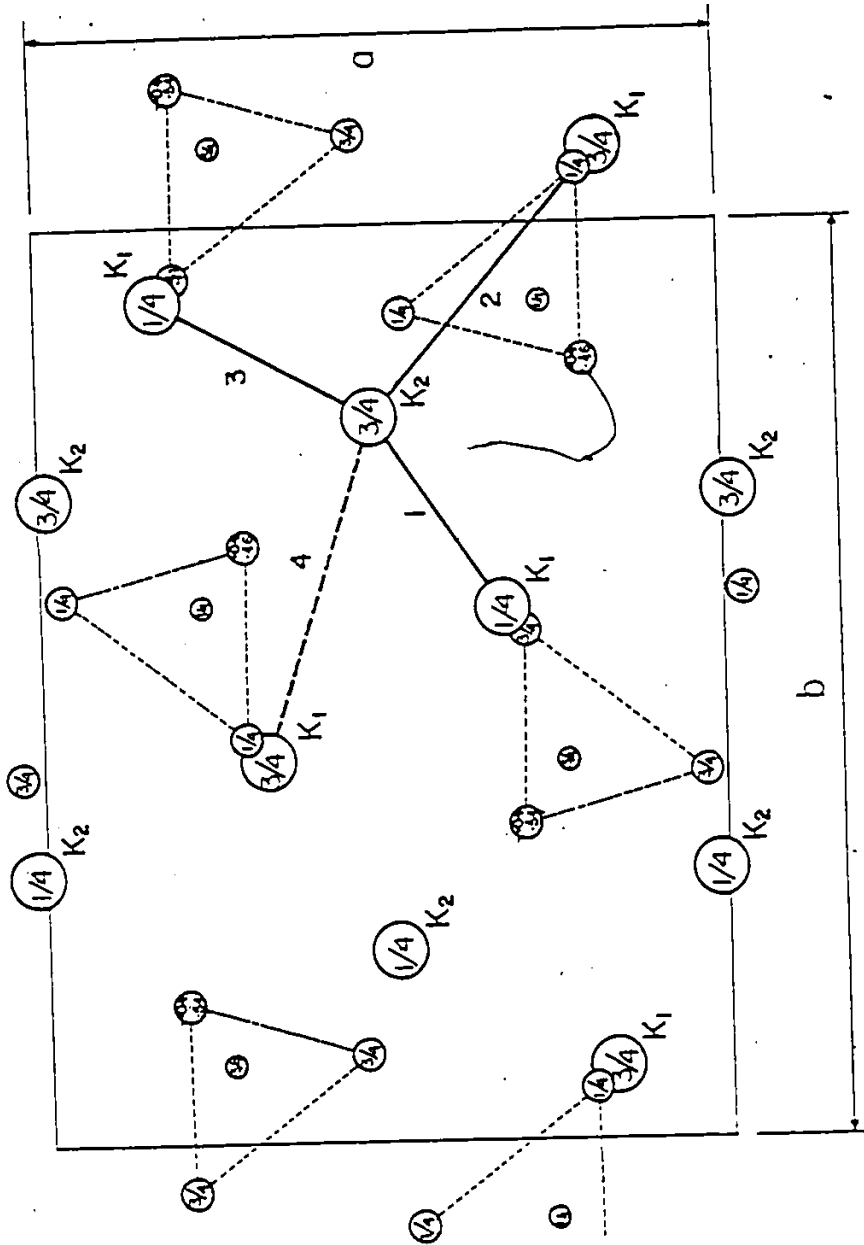
FIG VII.1
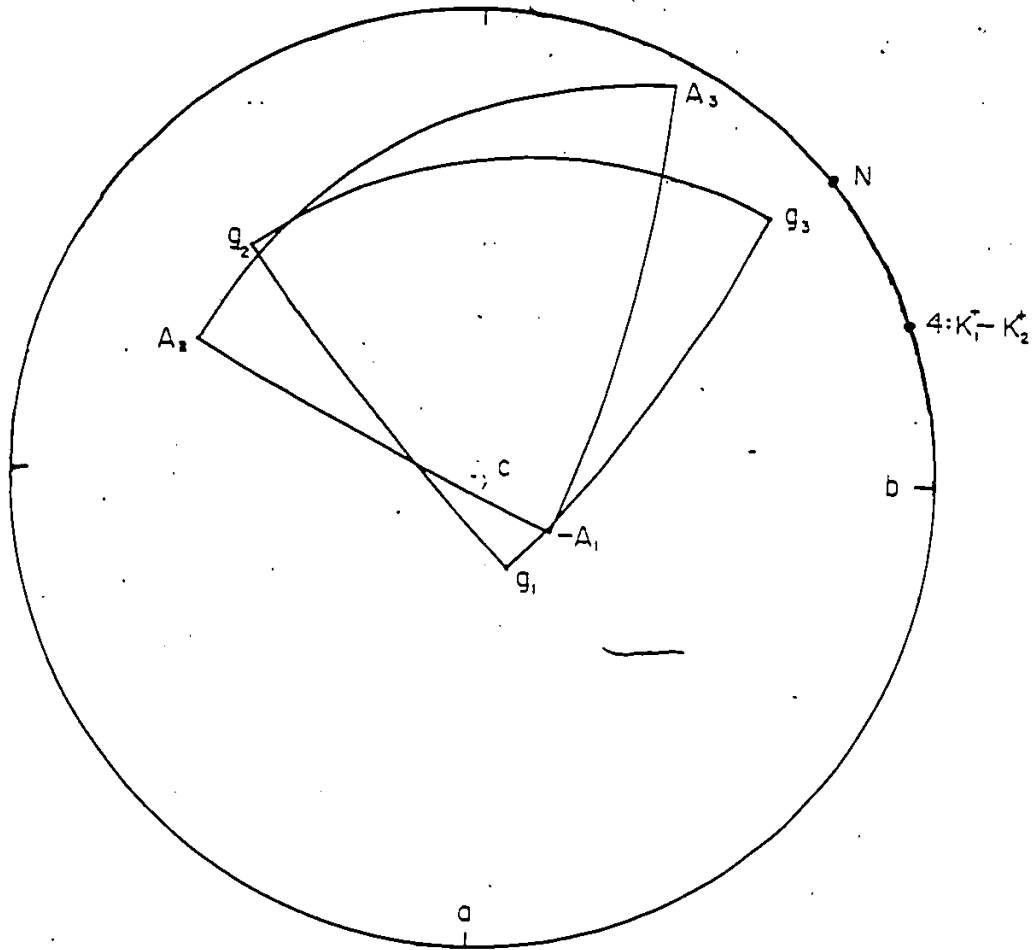
Stereogram of principal axes of g and A tensors with respect to crystallographic axes.

FIG VII.2

It is generally agreed that g is symmetric in the absence of an external electric field. If we assume that the g and A "tensor" can be adequately fitted by symmetric sets of parameters then g and A can be diagonalized (see appendix 10 for method) to yield the principal axes. These are shown on a stereogram in fig. VII.2 and the principal values tabulated in table VII.2 below. On the stereogram the principal directions of the g and A "tensors" are displayed as points joined by lines of 90°. The stereographic axes are those of the crystal and the line labelled 4 in fig. VII.1 is shown in the ab plane.

TABLE VII.2

g_1 2.122	A_1 55.3
g_2 2.052	A_2 -32.9
g_3 2.407	A_3 241.3
	$(\times 10^{-4} \ cm^{-1})$

As pointed out by Abragam and Bleaney[11] g and A are not time second rank tensors, rather gg and AA, however since we are taking both g and A to be symmetric diagonalizaing g necessarily diagonalizes gg etc., and so the principal axes and values are unchanged.

As can be seen from the stereogram clear non coincedences in g and A principal axes are observed particularly for g_3 and A_3. Fair corroboration of Abdulsavirov[1] can be seen with an angle of 22° between direction $K_2^+ - K_1^+ : 4$ and g_3. Even more significant is the fact that g_3 is within 9° of the nor-

mal to the rectangle formed by the remaining K_1 ligands nearest the vacancy. This is labelled N on the stereogram.

Freeman and Dilbrow[2] have also investigated K_2SO_4:Cu^{2+} and isostructural Rb_2SO_4:Cu^{2+} and have reported not only noncoincidences in g and A principal axes of $8°$ but also asymmetrics in A. They also cite five other recently reported cases of low symmetry. They only concentrated on centre type 1 as defined by Abdulsabirov[1] (direction 1 and fig. VII.1) and omitted a quadrupole term. However for our set of weak lines $M_I = \pm 1$ transitions varies greatly with direction.

Non-coincidence of g and A tensor is allowed whenever the point symmetry at a paramagnetic ion is monoclinic or triclinic but not for higher symmetrics. As fig. VII.2 shows we are clearly dealing here with a case of triclinic symmetry, since non-coincidences in excess of $12°$ for all axes are clearly demonstrated and there is no common principal axis which would result from monoclinic (C_2) or higher symmetry[12].

As discussed by Belford et al[12], for such low symmetry the A tensor need not be symmetric but the limitation with orientation dependent measurements on single crystals is that A_X, A_Y and A_Z (XYZ being the principal axis system of the A tensor) along with two Euler angles parameterizing the disposition of gg and AA can be measured, but A has nine independent components so that A cannot be completely characterized. In practical terms this means that even if A is genuinely asymmetric it may not be possible to detect asymmetrics.

On a molecular level the problem of the ground state may be very crudely approached by 1st order perturbation theory. It can be shown that a cubic environment with a tetragorial elorigation produces the energy level-scheme shown below in fig. VII.3.
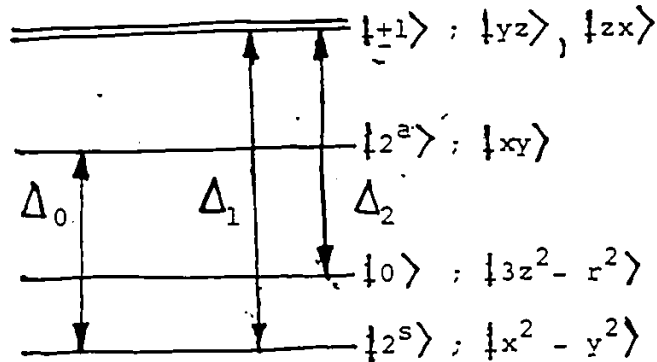
fig. VII.3

Spin orbit coupling cannot mix $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$ but mixes in some of the $|zx\rangle$ and $|xy\rangle$ to give an axial g tensor

$$g_{11} = 2 - \frac{8\lambda}{\Delta_0}$$

$$g_\perp = 2 - \frac{2\lambda}{\Delta_1}$$

This is in contrast to a $|3z^2 - y^2\rangle$ ground state which gives

$$g_{11} = 2$$

$$g_\perp = 2 - \frac{6\lambda}{\Delta_2}$$

This shows that we are dealing with a predominantly square-planor ground state ie. $|x^2 - y^2\rangle$ in the plane formed by the four coordinating K_1^+ sites with the normal N.A low symmetry crystal field however may mix $|x^2 - y^2\rangle$ with $|3z^2 - r^2\rangle$ and

the g values observed can be fitted to a 1st order pertorbation expression to give a ground state.

$$|g\rangle = \alpha(|x^2 - y^2\rangle + \beta|3z^2 - r^2\rangle)$$

with $\beta = 0.065$

In other words the effect of the vacancy is to mix in $|3z^2 - r^2\rangle$ with z pointing towards the vacancy.

Presumably this centre occurs less frequently for emergetic reasons and since the signal is proportional to the concentration of paramagnetic centres this allows a rought estimate of the relative occurence of the different centre types. This yields an occurence rate 0.3% that of the other centres which have signals of roughly equal strength.

At any rate the concluding remarks to be made from this investigation are to tentatively confirm the hypothesis of Abdulsabirov[1] and to report a case of Cu^{2+} occupying a low symmetry site resulting in non-coincidences in excess of 12° in $\tilde{gg}$ and $\tilde{AA}$ principal axes.

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48

APPENDIX 1

RESULTS

A right-handed coordinate system was chosen which coincided with the crystallographic axes for tabultation of results and input into the parameter fitting program. Polar coordinates were employed and the correspondence is shown below:

ϕ azimutal angle

θ polar angle

ϕ	θ	crystallographic axis
$0°$	$0°$	b
$0°$	$90°$	c
$90°$	$90°$	a

Computer printout of results is shown overleaf and the format is as follows

columns 1-4: ϕ

columns 5-8: θ

columns 9-14: ω_{DPPH} MHZ

columns 15-20: transition IF = 1 to JF = 8 MHZ

columns 21-26: transition IF = 2 to JF = 7 MHZ

columns 27-32: transition IF = 3 to JF = 6 MHZ

columns 33-38: transition IF = 4 to JF = 5 MHZ

```
 SJ.S     LIST    AKANAYRYYY  HMELL
         00003253336(541210(54796853202451783E5
         00001004352210872(97 5363421027562482694
         00003067537341027454627650103754324547
         000004413012250752043560421477560023597
         0000057265321207 4  7520715436727323A3
         0300047032107454 223720123507434025
         00000272513064  754213320373014307372
         00001446054201315647 795011704607703106
         00000247386542102669795204137326557054
         00001553358755402196336524475320154863
         00000204352012257699530215494532773805
         00001593362012025048759532105478523662
         09000402350107759532107400214375744533
         09001394361055473220760021435527573014
         09000305352103487542024451036078540c652
         090029737/55321074637301573 8590234617
         0900150353012667542106958820461753324
         04970900321054487932015466272214987063
         1303090003421037692353014558755861490092
         04460900342120865312735664000235817334
         1354009038607442102051744215073002305709
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         0155097038621047420501702750489105571003
         164400003352105687750043249651049572752c
         01250900352105445975215045662753253215P8
         167509003345054910700532634953735286541
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         00253703034201547027023546528701353120
         17750003335210977005740215347965432537001
         00030907032015459362507489730021547738654
         0300074735220014867520451036358792411233
         000010573624452790112357402136995752204
         00000705335542130633952741356520553741e2
```

//
//

APPENDIX 2

IDENTIFICATION OF CRYSTALLOGRAPHIC AXES

X-ray measurements were performed by Dr. M. Khan with the aid of his four circle diffractometer euabling identification of crystallographic axes. The diffractometer used the Syntex system. A photograph of forward scattering spots produced by the sample crystal is shown below.
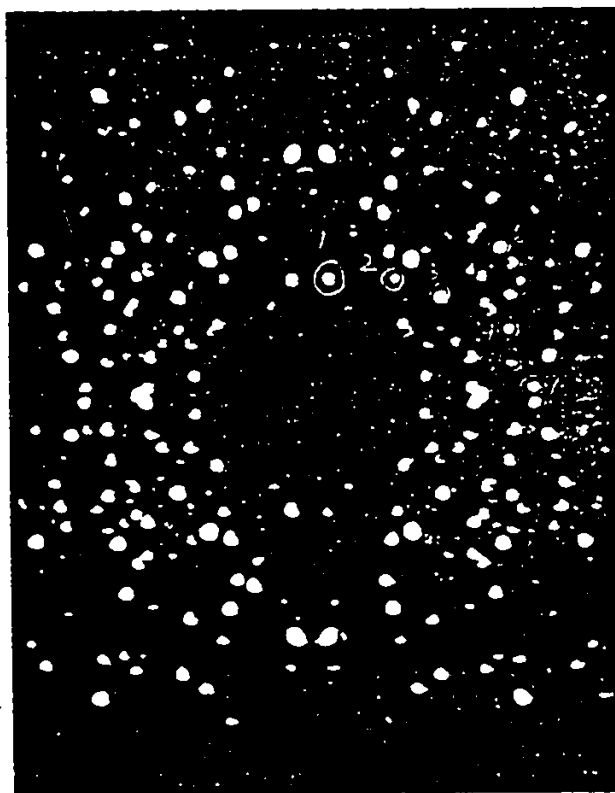
```
C                                                                      HAMF  40
C                                                                      HAMF 130
                                                                       HAMF 140
      IMPLICIT REAL*8(A-H,O-Z)
      COMPLEX*16 DCONJG,DH(36,14),DHT(36,14),EVECT(64 ),H(36 ),IMAG,ZERO
     1,CA(36),DDP(36),B(36)
      DIMENSION  A(6),             ,D1F(14),D2F(196),D2FINV(196),EN( 8),
     1 ALPHA(50),BETA(50),D(14), SIGMA(14) ,HO(50),IF(11),JF(11),F(12),
     2 GNAME(2),DE(14),HDP(50),HEADER(7),P(14),HB(50,11)
      DATA C1,C2/'GAUSS','10-4CM-1'/,IMAG/(0.D0,1.D0)/,ZERO/(0.D0,0.D0)/HA4F 160
C                                                                      HAMF 200
C              INPUT FORMAT STATEMENTS                                 HAMF 210
C                                                                      HAMF 220
  100 FORMAT(2I2,F6.1)                                                 HAMF 230
  101 FORMAT(2F5.1,3F10.7,2F10.3)
  102 FORMAT(I2,F5.1,I2/7A8,2A8)                                       HAMF 240
  103 FORMAT(8F10.5)
  104 FORMAT(16F5.1)                                                   HAMF 250
  106 FORMAT (8F10.7)
  107 FORMAT (3F10.7)
  108 FORMAT (5F10.5)
  110 FORMAT(4(8F10.6/),7F10.6/,2(5F10.6/),2F10.6)                     HAMF 280
  111 FORMAT(1X,12G10.3)
C                                                                      HAMF 290
C              OUTPUT FORMAT STATEMENTS                                HAMF 300
C                                                                      HAMF 310
  150 FORMAT(1H1,//25X,7A8,2A8)                                        HAMF 320
  152 FORMAT(///1X,'NUMBER OF ORIENTATIONS=',I2,5X,'NUMBER OF ITERATIONSHAMF 330
     1=',I2,5X,'TEMPERATURE(C)=',F6.1)                                 HAMF 340
  154 FORMAT(/1X,'SIZE OF MATRIX=',I2,5X,'SPIN VALUE=',F6.1,5X,'NUMBER  HAMF 350
     1OF PARAMETERS=',I2)                                              HAMF 360
  156 FORMAT(/1X,'DPPH(MHZ)',12F9.4)                                   HAMF 370
  158 FORMAT(/1X,'THETA:',2X,12(F7.1,2X))                              HAMF 380
  160 FORMAT(/1X,'PHI  :',2X,12(F7.1,2X))                              HAMF 390
  162 FORMAT(//45X,'*** SPECTRA(MHZ) ***')                            HAMF 400
  164 FORMAT(/10X,12(2X,F7.4))                                         HAMF 410
  166 FORMAT(//,1X,'PROTON MHZ TO GAUSS=',F7.3,15X,'DPPH G VALUE=',F8.6,HAMF 420
     1/,1X,'FREE ELECTRON G VALUE=',F8.6)                              HAMF 430
  168 FORMAT(1H1,//50X,'ITERATION #',I1///)                            HAMF 450
  169 FORMAT(14X,'GX',10X,'GY',10X,'GZ',10X,'GXY',9X,'GZX',9X,'GZY')
  170 FORMAT(14X,'AX',10X,'AY',10X,'AZ',10X,'AXY',9X,'AZX',9X,'AZY')
  171 FORMAT(14X,'QX',10X,'QY',10X,'QZ',10X,'QXY',9X,'QZX',9X,'QZY')
  172 FORMAT( 10X,6(2X,F10.5)/)
  174 FORMAT(////,5X,'THETA=',F6.1,5X,'PHI=',F6.1,//)                  HAMF 490
  176 FORMAT(23X,'TRANSITION',9X,'DEVIATION(GAUSS)')                   HAMF 500
  178 FORMAT(20X,I2,'/2',2X,'--',2X,I2,'/2',10X,G10.3)                 HAMF 510
  180 FORMAT(//50X,'PREDICTED DISPLACEMENTS'/,6X,'D(1)',6X,'D(2)',6X,'D(HAMF 520
     13)',6X,'D(4)',6X,'D(5)',6X,'D(6)',6X,'D(7)',6X,'D(8)',6X,'D(9)',  HAMF 530
     36X,'D(10)',5X,'D(11)',5X,'D(12)')
  181 FORMAT(2X,12F10.5)                                               HAMF 540
  182 FORMAT(6X,'D(13)',6X,'D(14)',6X,'D(15)',6X,'D(16)',6X,'D(17)',6X,'HAMF 550
     1D(18)')
  184 FORMAT(//50X,'NEW VALUES FOR PARAMETERS')
  186 FORMAT(//50X,'STANDARD DEVIATION FOR EACH PARAMETER')            HAMF 560
  188 FORMAT(10X,'VALUE OF ',I2,'TH PARAMETER IS NOT CONVERGENT')      HAMF 570
  190 FORMAT(//5X,'RMS DEVIATION=',F8.1,' GAUSS',10X,'NEW RMS DEVIATION=HAMF 580
     1',F8.1,' GAUSS',10X,'NUMBER OF LINES=',I3)                       HAMF 590
C                                                                      HAMF 660
C              READ INPUT DATA CARDS                                   HAMF 670
C                                                                      HAMF 680
 1000 CONTINUE
      READ 100,LM,ITM,TEMP                                             HAMF 690
      READ 102,N,SPIN,IMAX,HEADER,GNAME                                HAMF 700
      READ 108,PMHG,GDP,GFE                                            HAMF 760
      READ 106,(P(I),I=1,6)
      READ 106,(P(I),I=7,IMAX)
      READ 100, NCORE
      READ 1011,(IF(K),JF(K),K=1,11)
 1011 FORMAT(12(1X,2I1))
      PRINT 162
      IN=0
   10 IN=IN+1
      DO 199 K=1,12
  199 F(K)=0.0
      READ 1030,ALPHA(IN),BETA(IN),HO(IN),(F(K),K=1,10)
 1030 FORMAT(6X,2F4.1,12F6.4)
      IF(HO(IN).EQ.0.)GOTO30
      DO 20 K=1,11
      II=IF(K)
```

```
       JJ=JF(K)
   20  HB(IN,K)=F(K)*PMHG
       HDP(IN)=HC(IN)*PMHG*GDP/GFE
       PRINT 2005,IN,ALPHA(IN),BETA(IN),HO(IN),(IF(K),JF(K),F(K),K=1,8)
 2005  FORMAT('0',2X,I3,2F6.1,F7.4,2X,11(2I1,1X,F7.4))
       GO TO 10
   30  LM=IN-1                                                            HAMF 790
C                                                                         HAMF 800
C                   PRINT INPUT DATA                                      HAMF 810
C                                                                         HAMF 820
       PRINT 150,HEADER,GNAME                                             HAMF 830
       PRINT 152,LM,ITM,TEMP                                             HAMF 840
       PRINT 154,N,SPIN,IMAX
       PRINT 166,PMHG,GDP,GFE                                             HAMF 920
C                                                                         HAMF 930
C                   DEFINITIONS                                           HAMF 940
C                                                                         HAMF 950
       DR2=DSQRT(2.D0)                                                    HAMF 960
       IMAX2=IMAX*IMAX                                                    HAMF 970
       NN=(N+1)*N/2                                                       HAMF 980
C                                                                         HAMF 99
C              CORRECT AND CONVERT FIELD VALUES                           HAMF1000
C                                                                         HAMF1100
C              ITERATIONS LOOP STARTS HERE                                HAMF1110
C                                                                         HAMF1120
       DO 204 IT=1,ITM                                                    HAMF1130
       NL=0                                                               HAMF1140
C                                                                         HAMF1150
C                   INITIALIZATION                                        HAMF1160
C                                                                         HAMF1170
       XLSF=0.D0
       DO 207 IJ=1,NN
       H(IJ)=ZERO
       B(IJ)=ZERO
       DA(IJ)=ZERO
       DDP(IJ)=ZERO
       DO 207 J=1,IMAX
       DH(IJ,J)=ZERO
  207  DHT(IJ,J)=ZERO                                                     HAMF1180
       DO 206 IJ=1,IMAX2                                                  HAMF1190
  206  D2F(IJ)=0.D0                                                       HAMF1200
       DO 208 I=1,IMAX                                                    HAMF1210
  208  D1F(I)=0.D0                                                        HAMF1280
       PRINT 168,IT
       PRINT 169
       PRINT 172,(P(I),I=1,6)
       PRINT 170
       PRINT 172,(P(I),I=7,12)
       PRINT 171
       PRINT 172,(P(I),I=13,14)
C*******QUADRUPOLE TERM *******
       DO 402 LL=1,2
       ML=12+LL
  402  A(LL)=P(ML)
       CALL QUAD(B,A            )
       DO 404 LL=1,2
       DO 406 LO=1,2
  406  A(LO)=0.D0
       A(LL)=1.D0
       CALL QUAD(DA,A           )
       NX=12+LL
       DO 408 NA=1,36
  408  DH(NA,NX)=DA(NA)
  404  CONTINUE
C $$$$$$ SHFS TERM $$$$$$
       DO 403 LL=1,6
       ML=6+LL
  403  A(LL)=P(ML)
       CALL SHFS(DA,A           )
       DO 430 LL=1,36
  430  B(LL)=B(LL)+DA(LL)
       DO 405 LL=1,6
       DO 407 LO=1,6
  407  A(LO)=0.D0
       A(LL)=1.D0
       CALL SHFS(DA,A           )
       DO 409      NA=1,36
       NX=6+LL
```

54

```
400   DH(NA,NX)=DA(NA)
405   CONTINUE
C              SETTING UP FIELD INDEPENDENT COMPONENTS OF MATRIX ELEMENT    HAMF1
C              OF H(IAB) AND FIELD INDEPENDENT MATRIX ELEMENTS OF DH(IAB,   HAMF1
C              SET-UP THE A-MATRIX                                          HAMF1
C                                                                          HAMF1
C              TRANSITIONS LOOP STARTS HERE                                HAMF1
C                                                                          HAMF1
C              CALCULATE ENERGY DIFFERENCE FROM EXPERIMENTAL FREQUENCY     HAMF1
C              CALCULATE COMPONENTS OF FIELD VALUES                        HAMF1
C                                                                          HAMF1
      DO 222 L=1,LM
      THETAM  = BETA(L) *.0174533
      PHIM= ALPHA(L)*.0174533
      SINTH=DSIN(THETAM)
      COSTH=DCOS(THETAM)                                                   HAMF1
      SINPH=DSIN(PHIM)                                                     HAMF1
      COSPH=DCOS(PHIM)                                                     HAMF1
      X=COSPH*SINTH                                                        HAMF1
      Y=SINPH*SINTH                                                        HAMF1
      Z=COSTH                                                              HAMF1
      PRINT 174, BETA(L),ALPHA(L)
      PRINT 176                                                            HAMF1
303   NY=0
      DO 222 INDEX=1,11
      IF(HB(L,INDEX). LF.0.) GO TO 246
      HX=HP(L,INDEX)*X
      HY=HP(L,INDEX)*Y
      HZ=HP(L,INDEX)*Z
      NL=NL+1                                                              HAMF1
C                                                                          HAMF1
C              SETTING UP FIELD DEPENDENT MATRIX ELEMENTS OF H(IAB)        HAMF1
C                                                                          HAMF1
      DO 413 LL=1,6
413   A(LL)=B(LL)
      CALL HHAM(A,DA,HX,HY,HZ)
      DO 400 LL=1,36
400   H(LL)=DA(LL)+B(LL)
C     SET-UP THE DERIVATIVES OF THE S-MATRIX
      DO 412 LL=1,6
      DO 414 LOT=1,6
414   A(LOT)=0.00
      A(LL)=1.00
      CALL HHAM(A,DA,HX,HY,HZ)
      DO 415 NH=1,36
415   DH(NH,LL)=DA(NH)
412   CONTINUE
C                                                                          HAMF2
C              CALL CEIGEN DIAGONALIZE COMPLEX MATRIX H(IAB)               HAMF2
C              OBTAIN EIGEN VALUES  STORED DIAGONALLY IN H(IAB)            HAMF2
C              OBTAIN EIGENVECTORS STORED IN EVECT(IE)                     HAMF2
C                                                                          HAMF2
2500  FORMAT(6(2X,G12.6))                                                 HAMF2
      MV=0                                                                 HAMF2
      CALL CEIGEN (H,EVECT,N,MV)                                          HAMF2
      DO 236 K=1,N
      IAB=K*(K+1)/2
236   EN(K)=H(IAB) /2.00229                                              HAMF2
      KW=IF(INDEX)
      NK=JF(INDEX)
      DELTA=(EN(NK)-EN(KW))-HOP(L)
      M=IF(INDEX)
      K=JF(INDEX)
      PRINT 178,M,K,DELTA                                                 HAMF2
C                                                                          HAMF2
C              TRANSFORM DH(IAB,I) TO NEW BASIS                           HAMF2
C                                                                          HAMF2
703   MNM=1
      DO 243 I=1,IMAX
      DO 451 ID=1,36
451   DA(ID)=DH(ID,I)
      CALL STCM(DDP,DA,EVECT,N,KW,NK)
      DO 452 ID=1,36
452   DHT(ID,I)=DDP(ID)
243   CONTINUE
      XLSF=XLSF+(DELTA**2)
```

```
C
C
C
C              SETTING UP DF(INDEX.I)
C
      KKW=(KW*KW+KW)/2
      KWW=NK*(NK+1)/2
      DO 246 I=1,IMAX
      DF(I)=DHT(KWW,I)-DHT(KKW,I)
C
C          SETTING UP DIF/DF(I)
C
      DIF(I)=DIF(I)+(2*DELTA*DF(I))
  246 CONTINUE
  248 CONTINUE
C
C              SETTING UP D2F/DP(I)DP(J)
C
      DO 250 I=1,IMAX
      DO 250 J=1,IMAX
      IF(HP(L,INDEX).LE.0.0) GO TO 222
      IJ=I+(J-1)*IMAX
      D2E=0.D0
      DO 252 ID=1,N
      IF(ID.LT.KW) GO TO 256
      IF(ID.EQ.KW) GO TO 254
      KID=KW+(ID*ID-ID)/2
      DHTI=DCONJG(DHT(KID,I))
      DHTJ=DHT(KID,J)
      IF(ID.EQ.NK) GO TO 260
  254 IF(ID.LT.NK) GO TO 258
      KIDA=NK+(ID*ID-ID)/2
      DHTIA=DCONJG(DHT(KIDA,I))
      DHTJA=DHT(KIDA,J)
      GO TO 262
  256 KID=ID+(KW*KW-KW)/2
      DHTI=DHT(KID,I)
      DHTJ=DCONJG(DHT(KID,J))
      KIDA=ID+(NK*NK-NK)/2
      DHTIA=DHT(KIDA,I)
      DHTJA=DCONJG(DHT(KIDA,J))
      GO TO 262
  258 KIDA=ID+(NK*NK-NK)/2
      DHTIA=DHT(KIDA,I)
      DHTJA=DCONJG(DHT(KIDA,J))
      D2E=D2E+2.D0*DHTIA*DHTJA/(EN(NK)-EN(ID))
      GO TO 252
  260 D2E=D2E-2.D0*DHTI*DHTJ/(EN(KW)-EN(ID))
      GO TO 252
  262 D2E=D2E+2.D0*DHTIA*DHTJA/(EN(NK)-EN(ID))-2.D0*DHTI*DHTJ/
     1 (EN(KW)-EN(ID))
  252 CONTINUE
      D2F(IJ)=D2F(IJ)+(2.D0*DF(I)*DF(J))+D2E*DELTA
  250 CONTINUE
  222 CONTINUE
      NFREE=NL-IMAX
      XLSF=XLSF/NFREE
      DO 264 I=1,IMAX
      DIF(I)=DIF(I)/NFREE
      DO 264 J=1,IMAX
      IJ=I+(J-1)*IMAX
      D2F(IJ)=D2F(IJ)/NFREE
      D2FINV(IJ)=D2F(IJ)
  264 CONTINUE
C
C              CALCULATE AND PRINT PREDICTED DISPLACEMENTS D(I)
      PRINT 2000. (D2FINV(IJ),IJ=1,IMAX)
      PRINT 2000.(DIF(I),I=1,IMAX)
C
      CALL DMINV(D2FINV,IMAX,DET..)
 2000 FORMAT(2X,14G7.1)
      DO 266 I=1,IMAX
      IJ=I-IMAX
      D(I)=0.D0
      DO 266 J=1,IMAX
      IJ=IJ+IMAX
  266 D(I)=D(I)-D2FINV(IJ)*DIF(J)
      PRINT 10
```

```
  405   DH(NA,IX)=DA(NA)
  406   CONTINUE                                                               HAMF1310
C               SETTING UP FIELD INDEPENDENT COMPONENTS OF MATRIX ELEMENTSHAMF1320
C               OF H(IAB) AND FIELD INDEPENDENT MATRIX ELEMENTS OF DH(IAB,HAMF1330
C               SET-UP THE A-MATRIX                                          HAMF1340
C                                                                           HAMF1710
C               TRANSITIONS LOOP STARTS HERE                                HAMF1720
C                                                                           HAMF1730
C               CALCULATE ENERGY DIFFERENCE FROM EXPERIMENTAL FREQUENCY     HAMF1740
C               CALCULATE COMPONENTS OF FIELD VALUES                        HAMF1750
C                                                                           HAMF1760
       DO 222 L=1,LM
       THETAM = BETA(L) *.0174533
       PHIM= ALPHA(L)*.0174533                                              HAMF1800
       SINTH=DSIN(THETAM)                                                   HAMF1810
       COSTH=DCOS(THETAM)                                                   HAMF1820
       SINPH=DSIN(PHIM)                                                     HAMF1830
       COSPH=DCOS(PHIM)                                                     HAMF1840
       X=COSPH*SINTH                                                        HAMF1850
       Y=SINPH*SINTH                                                        HAMF1860
       Z=COSTH
       IF(IT.NE.ITW) GO TO 303
       PRINT 174, BETA(L),ALPHA(L)                                          HAMF1900
       PRINT 176
  303   KY=0
       DO 222 INDEX=1,11
       IF(HB(L,INDEX). LE.0.) GO TO 248
       HX=HB(L,INDEX)*X
       HY=HB(L,INDEX)*Y
       HZ=HB(L,INDEX)*Z                                                     HAMF1930
       NL=NL+1                                                              HAMF1970
C                                                                           HAMF1980
C               SETTING UP FIELD DEPENDENT MATRIX ELEMENTS OF H(IAB)        HAMF1990
C
       DO 410 LL=1,6
  410   A(LL)=P(LL)
       CALL HHAM(A,DA,HX,HY,HZ)
       DO 409 LL=1,36
  409   H(LL)=DA(LL)+H(LL)
C               SET-UP THE DERIVATIVES OF THE G-MATRIX
       DO 412 LL=1,6
       DO 414 LCT=1,6
  414   A(LCT)=0.D0
       A(LL)=1.D0
       CALL HHAM(A,DA,HX,HY,HZ)
       DO 416 NH=1,36
  416   DH(NH,LL)=DA(NH)
  412   CONTINUE                                                            HAMF2340
C                                                                           HAMF2350
C               CALL CEIGEN DIAGONALIZE COMPLEX MATRIX H(IAB)               HAMF2360
C               OBTAIN EIGEN VALUES  STORED DIAGONALLY IN H(IAB)            HAMF2370
C               OBTAIN EIGENVECTORS STORED IN EVECT(IE)                     HAMF2380
C
 2500  FORMAT(F(2X,D12.5))                                                  HAMF2390
       MV=0                                                                 HAMF2400
       CALL CEIGEN (H,EVECT,N,MV)                                           HAMF2430
       DO 235 K=1,N
       IAB=K*(K+1)/2
  236   EN(K)=H(IAB) /2.00229                                              HAMF2440
       KW=IF(INDEX)
       NK=JF(INDEX)
       DELTA=(EN(NK)-EN(KW))-HDF(L)
       W=IF(INDEX)
       K=JF(INDEX)
       IF(IT.NE.ITW) GO TO 304
       PRINT 176,M,K,DELTA                                                  HAMF2550
C                                                                           HAMF2560
C               TRANSFORM DH(IAB,I) TO NEW BASIS                            HAMF2570
C                                                                           HAMF2580
  304   NH=1
       DO 200 I=1, IMAX
       DO 451 IM=1, 36
  451   DA(I)=DH(IM,I)
       CALL STCH(DD,DA,EVECT,N,KW,NK)
       DO 452 I=1, 24
  452   DHT(I,I)=DD(IE)
```

```
240 CONTINUE
    XLSF=XLSF+(DELTA**2)                                            HAMF2750
C                                                                   HAMF2760
C                                                                   HAMF2770
C           SETTING UP DE(INDEX,I)                                  HAMF2780
C                                                                   HAMF2800
    KFW=(KV*KW+KW)/2                                                HAMF2805
    KKW=NK*(NK+1)/2                                                 HAMF2810
    DO 240  I=1,I4AX                                                HIMF2820
    DE(I)=DHT(KWW,I)-DHT(FKW,I)                                     HAMF2830
C                                                                   HAMF2840
C           SETTING UP DIF/DP(I)                                    HAMF2850
C                                                                   HAMF2860
    DIF(I)=DIF(I)+(2*DELTA*DE(I))                                   HAMF2870
245 CONTINUE                                                        HAMF2880
248 CONTINUE                                                        HAMF2890
C                                                                   HAMF2900
C           SETTING UP D2F/DF(I)DP(J)                               HAMF2910
C                                                                   HAMF2920
    DO 250 I=1,IMAX                                                 HAMF2930
    DO 250 J=1,IMAX
    IF(HF(L,INDEX).LE.0.0) GC TO 222                                HAMF2950
    IJ=I+(J-1)*IMAX                                                 HAMF2960
    D2E=0.0C                                                        HAMF2970
    DO 252 ID=1,N                                                   HAMF2980
    IF(ID.LT.KW) GO TO 256                                         HAMF2990
    IF(ID.EC.KW) GC TO 254                                         HAMF3000
    KID=KW+(ID*ID-ID)/2                                             HAMF3010
    DHTI=DCONJG(DHT(KID,I))                                         HAMF3020
    DHTJ=DHT(KID,J)                                                 HAMF3030
    IF(IJ.EC.NK) GO TO 260                                         HAMF3040
254 IF(IJ.LT.NK) GO TO 256                                         HAMF3050
    KIDA=NK+(ID*ID-ID)/2                                            HAMF3060
    DHTIA=DCONJG(DHT(KIDA,I))                                       HAMF3070
    DHTJA=DHT(KIDA,J)                                               HAMF3080
    GC TO 262                                                       HAMF3090
256 KID=ID+(KW*KW-KW)/2                                             HAMF3100
    DHTI=DHT(KID,I)                                                 HAMF3110
    DHTJ=DCONJG(DHT(KID,J))                                         HAMF3120
    KIDA=ID+(NK*NK-NK)/2                                            HAMF3130
    DHTIA=DHT(KIDA,I)                                               HAMF3140
    DHTJA=DCONJG(DHT(KIDA,J))                                       HAMF3150
    GC TO 262                                                       HAMF3160
258 KIDA=ID+(NK*NK-NK)/2                                            HAMF3170
    DHTIA=DHT(KIDA,I)                                               HAMF3180
    DHTJA=DCONJG(DHT(KIDA,J))                                       HAMF3190
    D2E=D2E+2.00*DHTIA*DHTJA/(EN(NK)-EN(ID))                        HAMF3200
    GC TO 262                                                       HAMF3210
260 D2E=D2E-2.00*DHTI*DHTJ/(EN(KW)-EN(ID))                         HAMF3220
    GC TO 252                                                       HAMF3230
262 D2E=D2E+2.00*DHTIA*DHTJA/(EN(NK)-EN(ID))-2.00*DHTI*DHTJ/       HAMF3240
   1 (EN(KW)-EN(ID))                                                HAMF3250
252 CONTINUE                                                        HAMF3260
    D2F(IJ)=D2F(IJ)+(2.00*DE(I)*DE(J))+D2E*DELTA                    HAMF3270
250 CONTINUE                                                        HAMF3380
222 CONTINUE                                                        HAMF3290
    NFREE=NL-IMAX                                                   HAMF3300
    XLSF=XLSF/NFREE                                                 HAMF3310
    DO 264 I=1,IMAX                                                 HAMF3320
    DIF(I)=DIF(I)/NFREE                                             HAMF3330
    DO 264 J=1,IMAX                                                 HAMF3340
    IJ=I+(J-1)*IMAX                                                 HAMF3350
    D2F(IJ)=D2F(IJ)/NFREE                                           HAMF3360
    D2FINV(IJ)=D2F(IJ)                                              HAMF3370
264 CONTINUE                                                        HAMF3380
C                                                                   HAMF3390
C           CALCULATE AND PRINT PREDICTED DISPLACEMENTS D(I)
    PRINT 2000, (D2FINV(IJ),IJ=1,IMAX2)
    PRINT 2000,(DIF(I),I=1,IMAX)
C                                                                   HAMF3400
    CALL MTINV(D2FINV,IMAX,DETER)                                   HAMF3410
2000 FORMAT(5X,14E12.1)
    DO 266 I=1,IMAX                                                 HAMF3420
    IJ=I-IMAX                                                       HAMF3430
    D(I)=0.00                                                       HAMF3440
    DO 266 J=1,IMAX                                                 HAMF3450
    IJ=IJ+IMAX                                                      HAMF3460
```

```
260 C(I)=D(I)-D2FINV(IJ)*D1F(J)                                              HAMF3470
    PRINT 180                                                               HAMF3480
    PRINT 181,(D(I),I=1,12)                                                 HAMF3490
    PRINT 182
    PRINT 181,(D(I),I=13,IMAX)
C                                                                           HAMF3500
C         CALCULATE AND PRINT NEW VALUES FOR PARAMETERS P(I)                HAMF3510
C                                                                           HAMF3520
                                                                           HAMF3530
    DO 203 I=1,IMAX                                                         HAMF3540
203 P(I)=P(I)+C(I)                                                          HAMF3550
    PRINT 184
    PRINT 169
    PRINT 172,(P(I),I=1,6)
    PRINT 170
    PRINT 172,(P(I),I=7,12)
    PRINT 171
    PRINT 172,(P(I),I=13,14)
    XLSNEW=XLSF                                                             HAMF3580
    II=-IMAX                                                                HAMF3590
    DO 270 I=1,IMAX                                                         HAMF3600
    II=II+IMAX+1                                                            HAMF3610
    XLSNEW=XLSNEW+D1F(I)*D(I)+(D2F(II)*C(I)*D(I))/2.D0                      HAMF3620
    JMIN=I+1                                                                HAMF3630
    IF(I.GE.IMAX) GO TO 270                                                 HAMF3640
    DO 272 J=JMIN,IMAX                                                      HAMF3650
    IJ=II-I+J                                                               HAMF3660
    XLSNEW=XLSNEW+D2F(IJ)*C(I)*D(J)                                         HAMF3670
272 CONTINUE                                                                HAMF3680
270 CONTINUE                                                                HAMF3690
C                                                                           HAMF3700
C         CHECK FOR CONVERGENCE OF P(I)                                     HAMF3710
C                                                                           HAMF3720
                                                                           HAMF3730
    II=-IMAX                                                                HAMF3740
    DO 274 I=1,IMAX                                                         HAMF3750
    II=II+IMAX+1                                                            HAMF3760
    IF (D2F(II).LT.0.D0) PRINT 188,I                                        HAMF3770
C                                                                           HAMF3780
C         CALCULATE SIGMA(I)                                                HAMF3790
C                                                                           HAMF3800
274 SIGMA(I)=DSQRT(DABS(D2FINV(II)*XLSNEW*2.D0/NFREE))                      HAMF3810
    RMS=DSQRT(XLSF)                                                         HAMF3820
    RMSNEW=DSQRT(XLSNEW)                                                    HAMF3830
    PRINT 186
    PRINT 169
    PRINT 172,(SIGMA(I),I=1,6)
    PRINT 170
    PRINT 172,(SIGMA(I),I=7,12)
    PRINT 171
    PRINT 172,(SIGMA(I),I=13,14)
    PRINT 190,RMS,RMSNEW,NL                                                 HAMF3850
204 CONTINUE                                                                HAMF3860
    IF (NCORE) 1000,1001,1000
1001 CONTINUE
    STOP                                                                    HAMF4200
    END                                                                     HAMF4210
```

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 storage is ues; the upper right side of the matrix
       actually stores: 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 diagon-
       alizes A. The colums of R are eigenvectors of A ordered
       as are the eigenvalues.

N -   the order (dimension) of A and R

MV -   input code:

                   0 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 Univer-
                  sity of Windsor for N = 4. The time will vary
                  roughly as N^4 but will be less if some off-dia-
                  gonal elements of A are initially = 0.

```
$JOB    LIST     XXXXXXXXX UNWIN
C                                                                      00004300
C     COMPUTES DOUBLE PRECISION EIGENVALUES AND. UNLESS MV=1. ALSO COMPLEX00004400
C     EIGENVECTORS OF THE HERMITEAN MATIX  CA   OF DIMENSION  N .        00004500
C     THE JACOBI METHOD IS USED.                                        00004600
C                                                                       00004700
C     THE CALLING PARAMETERS ARE                                        00004800
C     CA.  - THE HERMITEAN MATRIX TO BE DIAGONALIZED.  COMPACT STORAGE IS 00004900
C            USED.   NAMELY THE (I,J)TH ELEMENT OF THE UPPER RIGHT HALF OF 00005000
C            THE HERMITEAN MATRIX IS ELEMENT I+(J*J-J)/2 OF CA.          00005100
C            UPON RETURN.  CA  IS DIAGONALIZED WITH THE EIGENVALUES IN   00005200
C            ASCENDING ORDER ON THE DIAGONAL.                           00005300
C     CR   - THE INPUT VALUES OF THIS MATRIX ARE NOT USED. UPON RETURN, IF00005400
C            MV .NE. 1. CR CONAINS THE COMPLEX EIGENVECTORS OF THE INPUT 00005500
C            CA MATRIX.  THE EIGENVECTORS ARE STORED COLUMNWISE IN THE   00005600
C            SAME SEQUENCE AS THE EIGENVALUES.                           00005700
C     N    - THE DIMENSION OF THE MATRIX TO BE DIAGONALIZED.            00005800
C     MV   - IF EQUAL TO 1. ONLY EIGENVALUES AND NOT EIGENVECTORS ARE    00005900
C            COMPUTED.                                                   00006000
C                                                                       00006100
C     W. E. BAYLIS, PHYSICS, U. WINDSOR, WINDSOR, ONTARIO. FEB. 1972     00006200
C                                                                       00006300
C                                                                       00006400
      IMPLICIT REAL*8 (A,D,G,O-Z), CCMPLEX*16(C)                         00006500
      COMPLEX*16 ONE/(1.0D0.0.0D0)/,ZERO/(0.0D0.0.0D0)/                  00006600
      COMPLEX*16 DCONJG
      REAL*8 CDABS
      REAL*8 COSP.COSP2                                                  00006700
      DIMENSION CA(1),CR(1),CSINP(2)                                     00006800
C                                                                       00006900
C     CHECK DIMENSION                                                   00007000
C                                                                       00007100
      IF(N-1)1,2,5                                                       00007200
    1 PRINT 200,N                                                       00007300
  200 FORMAT(' ERROR. ATTEMPT TO DIMENSION CEIGEN BY N>'.I6.'.'/' STOP E00007400
     .XECUTICN.')                                                       00007500
      STOP                                                              00007600
    2 IF(MV .EQ. 1) GO TO 4                                             00007700
      CR(1) = ONE                                                       00007800
    4 RETURN                                                            00007900
C                                                                       00008000
C     GENERATE IDENTITY MATRIX                                          00008100
C                                                                       00008200
    5 RANGE = 1.0D-12                                                   00008300
      IF(MV .EQ. 1) GO TO 25                                            00008400
      IQ = -N                                                           00008500
      DO 20 J=1,N                                                       00008600
      IQ = IQ + N                                                       00008700
      DO 20  I=1,N                                                      00008800
      IJ = IQ + I                                                       00008900
      CR(IJ) = ZERO                                                     00009000
      IF(I .EQ. J) CR(IJ) = ONE                                         00009100
   20 CONTINUE                                                          00009200
C                                                                       00009300
C     COMPUTE INITIAL AND FINAL NORMS                                   00009400
C                                                                       00009500
   25 ANORM = 0.0D0                                                     00009600
      Y = 0.0D0                                                         00009700
      IJ = 0                                                            00009800
      DO 35 J=1,N                                                       00009900
      DO 35 I=1,J                                                       00010000
      IJ = IJ + 1                                                       00010100
      X = CA(IJ)*DCONJG(CA(IJ))                                         00010200
      ANORM = ANORM + X                                                 00010300
      IF(I .EQ. J) GO TO 35                                             00010400
      Y = Y + X                                                         00010500
   35 CONTINUE                                                          00010600
      ANORM = 1.414D0*DSQRT(ANORM)                                      00010700
      ANRMX = ANORM*RANGE/DFLOAT(N)                                     00010800
      IF(Y .LE. ANRMX) GO TO 165                                        00010900
C                                                                       00011000
C     INITIALIZE INDICATOES AND COMPUTE THRESHOLD.  :THR:               00011100
C                                                                       00011200
      IND = 0                                                           00011300
      THR = ANORM                                                       00011400
   45 THR = THR/DFLOAT(N)                                               00011500
   50 L=1                                                               00011600
   55 M=L+1                                                             00011700
      LQ = (L*L-L)/2                                                    00011800
      LL = LQ + L                                                       00011900
```

```
      ILQ = N*(L-1)                                        00012000
60  MJ = (M*M-M)/2                                         00012100
    LM = L + MQ                                            00012200
C                                                          00012300
C                                                          00012400
C   COMPUTE ELEMENTS OF 2X2 ROTATION MATRIX IF OFF-DIAGONAL ELEMENT IS  00012400
C   LARGER THAN THR                                        00012500
C                                                          00012600
      GAM = CDABS(CA(LM))                                  00012700
      IF(GAM .LT. THR) GO TO 130                           00012800
      MM = MQ + M                                          00012900
      IMQ = N*(M-1)                                        00013000
      IND = 1                                              00013100
      X = CA(LM)                                           00013200
      IF(X .LT. 0.0D0) GAM = -GAM                          00013300
      X = (CA(LL) - CA(MM))/2.0D0                          00013400
      Y = GAM/DSQRT(X*X+GAM*GAM)                           00013500
      IF(X .LT. 0.0D0) Y = -Y                              00013600
      SINP = Y/DSQRT(2.0D0*(1.0D0 + DSQRT(1.0D0 - Y*Y)))   00013700
      SINP2 = SINP*SINP                                    00013800
      COSP2 = 1.0D0 - SINP2                                00013900
      COSP = DSQRT(COSP2)                                  00014000
      CSINP(1) = GAM*SINP/CA(LM)                           00014100
      CSINP(2) = DCONJG(CSINP(1))                          00014200
      GSIN2P = 2.0D0*GAM*SINP*COSP                         00014300
C                                                          00014400
C                                                          00014500
C   ROTATE COLUMNS AND ROWS L AND M                        00014500
C                                                          00014600
      IQ = 0                                               00014700
      DO 125 I=1,N                                         00014800
      IQ = IQ + I - 1                                      00014900
      IF(I-M) 85,115,90                                    00015000
85  IM = I + MQ                                            00015100
      MCONJ = 1                                            00015200
      IF(I-L) 100,115,105                                  00015300
100 IL = I + LQ                                            00015400
      LCONJ = 1                                            00015500
      GO TO 110                                            00015600
90  IM = M + IQ                                            00015700
      MCONJ = 2                                            00015800
105 IL = L + IQ                                            00015900
      LCONJ = 2                                            00016000
110 CX = CA(IM)*CSINP(MCONJ)                               00016100
      CY = CA(IL)*CSINP(3-LCONJ)                           00016200
      IF(MCONJ .EQ. LCONJ) GO TO 112                       00016300
      CA(IL) = CA(IL)*COSP + DCONJG(CX)                    00016400
      CA(IM) = CA(IM)*COSP - DCONJG(CY)                    00016500
      GO TO 115                                            00016600
112 CA(IL) = CA(IL)*COSP + CX                              00016700
      CA(IM) = CA(IM)*COSP - CY                            00016800
115 IF(MV .EQ. 1) GO TO 125                                00016900
      ILR = ILQ + I                                        00017000
      IMR = IMQ + I                                        00017100
      CX = CR(ILR)*COSP + CR(IMR)*CSINP(1)                 00017200
      CR(IMR) = CR(IMR)*COSP - CR(ILR)*CSINP(2)            00017300
      CR(ILR) = CX                                         00017400
125 CONTINUE                                               00017500
      X = CA(LL)*SINP2 + CA(MM)*COSP2 - GSIN2P             00017600
      CA(LL) = CA(MM)*SINP2 + CA(LL)*COSP2 + GSIN2P        00017700
      CA(MM) = X                                           00017800
      CA(LM) = ZERO                                        00017900
130 IF(M .EQ. N) GO TO 140                                 00018000
      M = M+1                                              00018100
      GO TO 60                                             00018200
140 IF(L .EQ. N-1) GO TO 150                               00018300
      L = L+1                                              00018400
      GO TO 55                                             00018500
150 IF(IND .EQ. 0) GO TO 160                               00018600
      IND = 0                                              00018700
      GO TO 50                                             00018800
160 IF(THR .GT. ANRMX) GO TO 45                            00018900
C                                                          00019000
C   SORT EIGENVALUES AND EIGENVECTORS                      00019100
C                                                          00019200
165 IQ = -N                                                00019300
      LL=0                                                 00019400
      DO 185  I = 1,N                                      00019500
      IQ = IQ + N                                          00019600
      LL = LL + I                                          00019700
      JQ = N*(I-2)                                         00019800
      X = CA(LL)                                           00019900
```

```
      DO 185 J=I,N                                  00020000
      JQ = JQ + N                                   00020100
      MM = (J*J+J)/2                                00020200
      Y= CA(MM)                                     00020300
      IF(X .LE. Y) GC TC 185                        00020400
      CA(LL) = Y                                    00020500
      CA(MM) = X                                    00020600
      X = Y                                         00020700
      IF(MV .EQ. 1) GO TO 185                       00020800
      DO 180  K=1,N                                 00020900
      ILR = IQ + K                                  00021000
      IMR = JQ + K                                  00021100
      CX = CR(ILR)                                  00021200
      CR(ILR) = CR(IMR)                             00021300
  180 CR(IMR) = CX                                  00021400
  185 CONTINUE                                      00021500
      RETURN                                        00021600
      END                                           00021700
//
//
```

```
$JOB     LIST    XXXXXXXXX UNWIN
1        SUBROUTINE DGMPRC(A,B,R,N,M,L)
2        IMPLICIT REAL(A-H,O-Z)
3        DIMENSION A(144),E(144),R(144)
4        IR=0.DO
5        IK=-M
6        DO 10 K=1,L
7        IK=IK+M
8        DO 10 J=1,N
9        IR=IR+1
10       JI=J-N
11       IB=IK
12       R(IR)=0.DO
13       DO 10 I=1,M
14       JI=JI+N
15       IB=IB+1
16   10  R(IR)=R(IR)+A(JI)*B(IB)
17       RETURN
18       END
//
//
```

```
//W     JOB    (U10200S538),CLASS=W                    JOB 787
//W     JCB    (U10200S538),CLASS=W                    JOB 787
```

APPENDIX 8

DIAGONALIZATION OF g and A TENSORS

The computer program used to evaluate the principal axes and values of the g and A tensors is shown overleaf. The program forms a traceless tensor and them employs three votations to diagonalize this tensor.

```
         $JOB    WATF IV '>>>>>>>>>>,KP=26 F HELLS
   1            DIMENSION G(3),D(3),C(3,3),U(3,3),VV(3)
   2         20 READ 3,XX,YY,ZZ,XY,ZX,YZ
   3          3 FORMAT (8F10.5)
   4            XZ=ZX
   5            YX=XY
   6            ZY=YZ
   7            PRINT 3,XX,YY,ZZ,XY,XZ,ZY
   8            PI=180./57.296
   9            P=-(XX+YY+ZZ)
  10            Q=(XY*YY+XX*ZZ+YY*ZZ-YZ**2-XY**2-XZ**2)
  11            R=-(XX*ZZ*YY+2.*XY*YZ*ZX-YZ**2*XX-XY**2*ZZ-ZX**2*YY)
  12            A=(3.*Q-P**2)/3.
  13            A=-A
  14            B=(2.*A**3-9.*P*Q+27.*R)/27.
  15            PP=-B
  16            PP=ABS (PP)
  17            CO=(PP/2.)*(SQRT((3./A)**3))
  18            SI=SQRT (1.-CO**2)
  19            CS=ABS (CO)
  20            PHI=ATAN (SI/CS)
  21            IF(CO) 50,51,51
  22         50 PHI=PI-PHI
  23         51 ALPHA=PHI/3.
  24            AA=2.*SQRT (A/3.)
  25            G(1)=AA*COS (ALPHA-2.*PI*1./3.)
  26            G(2)=AA*COS (ALPHA-2.*PI*2./3.)
  27            G(3)=AA*COS (ALPHA-2.*PI*3./3.)
  28            PHI=PHI*57.296
  29            ALPHA=ALPHA*57.296
  30            AS=-P/3.
  31            PRINT 1,G(1),G(2),G(3),AS
  32            G(1)= (G(1)-P/3.)
  33            G(2)= (G(2)-P/3.)
  34            G(3)= (G(3)-P/3.)
  35            DO 10 L=1,3
  36            D(1)=XY*YZ-ZX*(YY-G(L))
  37            D(2)=ZX*XY-YZ*(XX-G(L))
  38            D(3)=(XX-G(L))*(YY-G(L))-XY**2
  39            DD=SQRT (D(1)**2+D(2)**2+D(3)**2)
  40            U(1,L)=D(1)/DD
  41            U(2,L)=D(2)/DD
  42         10 U(3,L)=D(3)/DD
  43            PRINT 1,G(1),G(2),G(3),PHI,ALPHA
  44            DO 11 N=1,3
  45         11 PRINT 1,U(1,N),U(2,N),U(3,N)
  46            DO 12 L=1,3
  47            DO 13 N=1,3
  48            SI=SQRT (1.-U(N,L)**2)
  49            C(N,L)=ATAN (SI/U(N,L))
  50            C(N,L)=C(N,L)*57.296
  51         13 CONTINUE
  52            VV(1)=U(1,L)
  53            VV(2)=U(2,L)
  54            VV(3)=U(3,L)
  55            TANA=ABS (VV(2)/VV(1))
  56            ALPHA=ATAN (TANA)
  57            IF(VV(1))101,100,100
  58        100 IF(VV(2))104,105,105
  59        104 ALPHA=-ALPHA
  60        105 GO TO 107
  61        101 IF(VV(2))102,103,103
  62        102 ALPHA=-180./57.296+ALPHA
  63            GO TO 107
  64        103 ALPHA= 180./57.296-ALPHA
  65        107 WW=ABS (VV(3))
  66            TANB=SQRT (1.-VV(3)**2)/WW
  67            BETHA=ATAN (TANB)
  68            IF(VV(3)) 108,109,109
  69        108 BETHA=180./57.296-BETHA
  70        109 BETHA=BETHA*57.296
  71            ALPHA=ALPHA*57.296
  72            PRINT 1,(C(N,L),N=1,3),ALPHA,BETHA
  73         12 CONTINUE
  74          1 FORMAT(25X,8F10.5)
  75            STOP
  76            END
```

        $ENTRY
 2.00569   2.01210   2.04221   0.00511   0.00755   0.01354

VITA AUCTORIS

I was born in Loughborough, Leicestershire, in 1959.
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Page 67 missing