PART I
AN ELECTRON SPIN RESONANCE STUDY OF RADICALS IN IRRADIATED SINGLE CRYSTALS OF MANDELIC ACID

PART II
A GENERALIZATION OF METHODS FOR DETERMINING g TENSORS

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
WILLIAM GEORGE WALLER
1973

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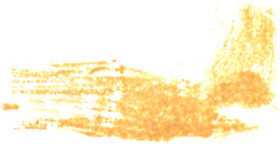

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ABSTRACT

PART I

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PART II

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DETERMINING g TENSORS

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In Part I, the electron spin resonance spectra of irradiated single crystals of mandelic acid, $C_6H_6CHOHCOOH$, have been studied. Two radicals, α-hydroxybenzyl ($C_6H_5\dot{C}HOH$) and cyclohexadienyl-glycolic acid ($C_6H_6CHOHCOOH$), were identified and the ESR parameters determined for each.

The α-hydrogen hyperfine splitting tensor of the α-hydroxybenzyl radical is nearly isotropic with principal values (-15.0,-15.3,-18.3) gauss and the g tensor is nearly isotropic with principal values (2.0022,2.0033,2.0039). The ESR data are those expected for a planar π-electron radical and molecular orbital calculations (INDO method) confirm this and provide detailed geometry. The benzene rings appear to have reoriented upon irradiation.

The cyclohexadienyl-glycolic acid radical shows a large hyperfine splitting by the methylene protons; the tensor is nearly axially symmetric and quite anisotropic, with principal values (-28.5,-52.5,-57.3) gauss.

In Part II, a generalization of the usual methods for obtaining the principal values, and directions of the principal axes, of the g tensor from single-crystal ESR data has been derived. The formalism of Part II converts the inherent overspecification of tensor elements into a determination of three rotational misalignments, and so improves the accuracy of the g-tensor parameters. The procedures developed have been applied to the determination of g tensors from rotations about orthogonal axes, monoclinic axes, coplanar axes, or general axes. The coplanar and general cases should prove useful in determining g tensors for needle-shaped crystals and for crystals with inconvenient face development. The equations have been cast in a convenient form for computer programming and a program has been written.

PART I

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Part II

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William George Waller

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics
Program in Chemical Physics

1973

To

My Parents

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Professor M. T. Rogers for his expert guidance and interest, and for the freedom allowed during this investigation. The author also wishes to thank Dr. S. Subramanian of the Indian Institute of Technology, Madras, India for helpful discussions and for obtaining the ENDOR spectra.

The aid of the following people is gratefully acknowledged: Mr. George Giddings for performing the γ-irradiations, Dr. A. Tulinsky for use of the x-ray equipment, Dr. M. Neuman for guidance in the crystallographic interpretation, and Dr. R. Lloyd of the University of Connecticut for useful discussions.

The author would like to thank the Atomic Energy Commission for financial support during the course of this study.

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PART I

AN ELECTRON SPIN RESONANCE STUDY OF RADICALS IN IRRADIATED SINGLE CRYSTALS OF MANDELIC ACID

INTRODUCTION

One distinctive difference between quantum mechanical and classical properties of systems is that there are sharply defined energy levels in the former as compared to a continuous range in the latter. In situations where the quantum mechanical energy levels are not too close together, a resonance technique can sometimes allow an accurate determination of energy differences between levels.

There are at least four "simple" types of resonance phenomena--nuclear, paramagnetic, ferromagnetic, and antiferromagnetic. The first is concerned with interactions of the nuclear dipoles, while the last three deal with electron dipoles. The last two phenomena deal with magnetic systems where the electron dipoles are strongly coupled by exchange forces. Paramagnetic resonance is confined to loosely-coupled systems where the paramagnetic units may be regarded as individuals.

Such loosely-coupled paramagnetic species sometimes can be formed in irradiated single crystals. The damaged molecules can become trapped and oriented in the crystal. The interaction of the odd electron with nuclei

in the damaged molecule would cause its energy levels to change and divide. These effects can be determined by electron spin resonance (ESR) spectroscopy and can be used to identify the radical and its orientation. Molecular information concerning the radical also can be deduced.

While there has been a lot of work done on ESR studies of aliphatic radicals in organic single crystals, the literature on ring compounds is small. There has been an interest in discovering the benzyl radical or a simple modification of it in single crystals. The nature of the delocalization of the unpaired electron could provide information concerning the structure of the radical. dl-Mandelic acid was chosen because it is a relatively simple ring system. On irradiation, two ring structures, the alpha-hydroxybenzyl radical and the cyclohexadienyl-glycolic acid radical, appear to be formed. The analysis of the ESR spectra of these radicals has been carried out and their geometrical and electronic structures are discussed in Part I of this thesis.

Part II of this thesis consists of a theoretical treatment of methods for determining g tensors. A generalized procedure is derived that can be applied to any symmetric second rank tensors such as the zero-field splitting and hyperfine interaction tensors $\overline{\overline{D}}$ and $\overline{\overline{A}}$, respectively. The computer programs used for Part I and Part II are also listed in the Appendices.

HISTORICAL BACKGROUND

I. History

Some important dates in the history of magnetic reasonance are as follows:

1936--First prediction of magnetic resonance absorption by Gorter.[1]

1938--First observation of magnetic resonance absorption in molecular beams by Rabi, Zacharias, Millman and Kusch.[2]

1945--First observation of the electron spin resonance phenomenon in liquids by Zavoisky.[3]

1946--First report of nuclear magnetic resonance by Purcell, Torrey and Pound[4] and by Bloch, Hansen and Packard.[5]

1947--First ESR free radical spectrum was observed by Kozyrev and Salikhov.[6]

1949--First report of ESR hyperfine structure by Penrose.[7]

1949--First evidence of quadrupole interaction by Ingram.[8]

1949--First ESR study of naturally occurring organic free radicals by Holden, Kittel, Merritt and Yager.[9]

1951--First analysis of the hyperfine structure in the ESR spectra of paramagnetic salts by Abragam and Pryce.[10]

1951--First ESR study of free radicals formed by radiation damage by Schneider, Day and Stein.[11]

1956--First ESR study of oriented organic radicals in a single crystal by Uebersfeld and Erb.[12]

1956--First ENDOR experiment by Feher.[13]

1958--First ESR study of a triplet state by Hutchison and Mangum.[14]

1959--First complete analysis of the ESR spectrum of an oriented organic radical in a single crystal matrix by Cole, Heller and McConnell,[15] by Ghosh and Whiffen,[16] and by Miyagawa and Gordy.[17]

II. ESR Literature

There are many surveys of the ESR literature[18-31] including in particular an early review by Morton[26] of radicals in single crystals. Recent work on ESR of organic radicals is discussed in a review by Kochi and Krusic.[31] There are also frequent review articles in the Annual Reviews of Physical Chemistry[32] and in the Annual Reports of the Chemical Society.[33] Other sources of information include the proceedings of ESR symposia[34-38] and collections of ESR data.[39,40]

There are also a large number of books on ESR. Textbooks giving a complete introduction to magnetic resonance are those by Carrington and McLachlan[41] and by Wertz and Bolton.[42] ESR theory is presented in a new book by Poole and Farach.[43] A more mathematical book with emphasis on interaction mechanisms was written by Slichter.[44] There is a comprehensive reference book by Abragam and Bleaney[45] that does not contain many formula derivations. A textbook approach in deriving the necessary mathematics for ESR theory has been used in a work by Griffith.[46] Comprehensive books covering the experimental techniques include those by Poole[47] and by Alger.[48]

III. g and A Tensors

In ESR, the most commonly measured quantities are the g and A tensors in crystals or their isotropic values in liquids, powders, or glasses. These quantities are defined by their contribution to the following spin Hamiltonian.

$$\mathcal{H} = \beta \vec{H} \cdot \bar{\bar{g}} \cdot \vec{S} + \sum_p \vec{I}_p \cdot \bar{\bar{A}}_p \cdot \vec{S}$$

where $\vec{H}$ is the magnetic field intensity vector, and $\vec{I}_p$ and $\vec{S}$ are the spin angular momentum vectors of the p^{th} nucleus and the unpaired electron, respectively. Given a specific magnetic field direction, the value of the g tensor describes the Zeeman contribution to the energy of the system as a linear function of magnetic field strength. The "shape" of the tensor describes the variation of this

Zeeman energy as a function of magnetic field direction in the crystal. In a similar manner, the A_p tensor describes the hyperfine energy contribution due to the interaction of the unpaired electron with the magnetic moment of the p^{th} nucleus.

The g and A_p tensors each have three principal values associated with three orthogonal directions. These principal values can be equivalently specified by their average isotropic part and their anisotropy.

From ESR studies of a variety of oriented radicals, investigators have found patterns in the average values and anisotropies of the g and A tensors. These are useful in identifying the radical. The principal g values are related to the orbitals occupied by the free electron. The principal values of $\bar{\bar{A}}_p$ are related to the number of bonds and the geometry between the p^{th} nucleus and the site where the electron is located.

IV. Pi-Electron Radicals

One of the common types of organic radicals, concerning which there is a great deal of theoretical and experimental literature, is the pi-electron radical. This is a paramagnetic molecule containing a number of coplanar atoms, usually carbon and hydrogen, such that the spin paramagnetism is largely distributed in atomic orbitals having a node in the molecular plane. The experimental A_p tensors have been related to the interaction between

the unpaired electron and α protons ($\dot{C}$-H_α), β protons ($\dot{C}$-C-H_β) and ^{13}C of the central carbon atom.

For the α protons, the theoretical relationship for the isotropic part of $\overline{\overline{A}}$ is[28, 49-54]

$$a_{H_\alpha} = Q\rho_\pi$$

where Q is approximately a constant having a value of -22.5 gauss and ρ_π is the π-electron spin density on the carbon atom. The anisotropic part has been found in general to consist of the three principal values (+10,0,-10) gauss. The first value corresponds to the H-C bond direction, the second value to a direction perpendicular to the radical plane, and the third value to a direction perpendicular to the two previous directions.[26, 55, 56]

The $\overline{\overline{A}}$ tensor for β protons is generally quite isotropic and has been described by the equation[57, 58]

$$a_{H_\beta} = B_O + B_2 \cos^2 \theta$$

where B_O is a constant with a value between 0 and 4 gauss, B_2 is about 50 gauss, and θ is the angle between the projections of the axis of the unpaired electron π orbital and the C-H_β bond onto a plane perpendicular to the C-C bond. Tables of α- and β-proton splittings have been given in the Ph.D. theses of Kispert[59] and Watson.[60]

THEORETICAL

I. Introduction

The theoretical development and the inherent limitations of ESR are dependent upon the approximations used to solve the nonrelativistic Schroedinger equation

$$\mathcal{H}\Psi = E\Psi. \tag{1}$$

The problem is that Ψ is a function of the positions, momenta, and spin states of <u>all</u> the particles in the system. The Hamiltonian $\mathcal{H}$ is a quantum mechanical operator analogous to the classical mechanical formula for the total energy of the system. This is complex in that it includes all interactions between the particles. The main approximation needed to solve Equation (1) is taken from the following equation:

$$\Psi = \sum_{i=0}^{\infty} c_i \psi_i, \tag{2}$$

where ψ_i are the functions which (as is postulated) span the space. We assume that we can pick some set of functions ϕ_i so that the infinity in the summation is replaced by a finite reasonably small number.

If Equation (2) is applied in a perturbation formalism where

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \ , \ \mathcal{H}_0 \phi_0^{(j)} = E_0 \phi_0^{(j)} \ , \tag{3}$$

and the effect of $\mathcal{H}'$ is small compared to that of $\mathcal{H}$, then the coefficients c_i of Equation (2) are of the order of $(E_0^{(k)} - E_o^{(j)})^{-n}$ for the n^{th} order perturbation where $E_0^{(k)}$ and $E_0^{(j)}$ are the exact energies in Equation (3). So if we order the functions $\phi_0^{(j)}$ according to their energies $E_0^{(j)}$, then we terminate the summation in Equation (2) when $E_o^{(j)}$ becomes "large" since that corresponding coefficient is "small." The functions ϕ_i that we choose form a manifold in the infinite dimensional ψ_i vector space.

Electron spin resonance is concerned with the interaction of an electron with other electrons, nuclei, and external magnetic fields. The number of functions needed in the manifold to describe reasonably this interaction is determined by considering the time-reversal operator and Kramers theorem.

II. Time Reversal and Kramers Degeneracy

The time-reversal operator θ can be defined by its effect on wave functions ψ_i in

$$\frac{\partial(\theta\psi_i(t))}{\partial t} = - \frac{\partial \psi_i(t)}{\partial t} \ .$$

Thus θ would have the effect of reversing every momentum while not affecting the positions of the particles. We, therefore, can define θ by its effect on operators:[61]

$$\theta x \theta^{-1} = x \; ; \; \theta p_x \theta^{-1} = -p_x \; . \tag{4}$$

We can apply this similarity transformation to the quantum mechanical operators that correspond to the following classical quantities:[62]

$$\vec{L} = \int m\vec{r}x\vec{v} \, d\tau \; , \qquad \vec{\mu} = \frac{1}{2c}\int \vec{r}x\vec{J}(\vec{r}') \, d\tau \; ,$$

$$\vec{H}(\vec{r}) = \frac{1}{c}\nabla x \int \frac{\vec{J}(\vec{r}')}{|\vec{r}-\vec{r}'|} \, d\tau \; ,$$

where $\vec{L}$ is the angular momentum, and $\vec{\mu}$ and $\vec{H}$ are the magnetic moment and magnetic field, respectively, of the current distribution $\vec{J}(\vec{r}')$. We can thus write in terms of operators

$$\theta\vec{L}\theta^{-1} = -\vec{L} \; , \; \theta\vec{\mu}\theta^{-1} = -\vec{\mu} \; , \; \theta\vec{H}\theta^{-1} = -\vec{H} \; , \; \theta\vec{S}\theta^{-1} = -\vec{S} \; , \tag{5}$$

where the last relationship follows from the exact mathematical analogue of the postulated intrinsic spin to the angular momentum in quantum mechanics.

It can be seen then that the spin-spin and spin-orbital interactions of the electrons are invariant with respect to the time-reversal similarity transformation, as is the kinetic energy and any time-independent potential energy. If these are the only terms we allow in the

Hamiltonian of the isolated system of the electron, then we see that $\theta\mathcal{H}\theta^{-1} = \mathcal{H}$, and θ is a symmetry element.

Consider the following equations:

$$(i\hbar\frac{\partial}{\partial t})\psi = \mathcal{H}\psi \tag{6}$$

$$\theta(i\hbar\frac{\partial}{\partial t})\psi = (\theta\mathcal{H}\theta^{-1})\theta\psi$$

$$\theta(i\hbar\frac{\partial}{\partial t})\psi = \mathcal{H}\theta\psi \ . \tag{7}$$

They can be taken to mean that the isolated system evolves forwardly in time (Equation (6)) in the same way as it would appear if viewed by someone going backwards in time (Equation (7)). Continuing the physical reasoning, we would deduce that the transition probabilities between states is the same in the time-forward or time-backwards view of the system. This gives us the mathematical assumption that

$$|(\Phi,\Psi)|^2 = |(\theta\Phi,\theta\Psi)|^2.$$

Using this equation, it is shown[63] that

$$\theta\sum_i a_i\psi_i = \sum_i a_i^*\theta\psi_i \ ; \ \theta^2 = \pm 1 \tag{8}$$

and thus we call θ an antilinear operator. From Equation (4), θ has been determined for a one-electron system in the coordinate representation

$$\theta = i\sigma_y K_0 = \zeta K_0 = K_0\zeta \ ,$$

where we use the standard Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} ,$$

and we define

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \zeta = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad K_0 \psi \equiv \psi^* ,$$

which can be used to derive

$$\theta^{-1} = -K_0 \zeta = -\zeta K_0 \; ; \quad \zeta^2 = \theta^2 = -1$$

and the formulas for the many-electron system

$$\theta = K_0 \prod_{p=1}^{n} \zeta_p \; ; \; \theta^{-1} = K_0 \prod_{p=1}^{n} (-\zeta_p) ,$$
$$\theta^2 = (\pm) 1 \text{ if } n \text{ is } \begin{pmatrix} \text{even} \\ \text{odd} \end{pmatrix}. \tag{9}$$

If an isolated system has an odd number of electrons, then $\theta^2=-1$ from Equation (9), and it has been shown[64] that if ψ is an eigenfunction, then $\Phi = \theta\psi$ is another orthogonal eigenfunction of the same energy. The ground state of the isolated system of the electrons is then at least two-fold degenerate and this two-dimensional space is spanned by what is called the Kramers doublet.

If we now add to the Hamiltonian the interaction due to an <u>external</u> magnetic field $\vec{\mu}\cdot\vec{H}_{ext}$, then $\mathcal{H}$ is not invariant under the θ similarity transformation because

$$\theta(\vec{\mu}\cdot\vec{H}_{ext})\theta^{-1} = (\theta\vec{\mu}\theta^{-1})\cdot(\theta\vec{H}_{ext}\theta^{-1})$$

$$= (-\vec{\mu})\cdot(\vec{H}_{ext}\theta\theta^{-1}) = -\vec{\mu}\cdot\vec{H}_{ext}$$

and $\vec{H}_{ext}$ is not part of the isolated system under study. Likewise, if the nucleus has a magnetic moment, than $\vec{\mu}_I \cdot \vec{H}_{el}$ is <u>not</u> invariant because

$$(\theta\vec{\mu}_I\theta^{-1})\cdot(\theta\vec{H}_{el}\theta^{-1}) = (\vec{\mu}_I)\cdot(-\vec{H}_{el}) \quad , \tag{10}$$

where $\vec{\mu}_I$ is the magnetic moment of the nucleus (which is <u>not</u> part of the system) and $\vec{H}_{el}$ is the magnetic field produced by the electrons at the nucleus.

In ESR, these interactions are considered perturbations which lift the degeneracy of the Kramers doublet and thus we assume that the excited states of the electron system are much higher in energy than either of the external interactions.

III. <u>g and A Tensors</u>

The g tensor is developed by considering the matrix elements of $\vec{\mu}$. It has been shown[64] that, since $\theta\vec{\mu}\theta^{-1}=-\vec{\mu}$ from Equation (5), the expectation values of $\mu_q(q=x,y,z)$ in the two Kramers-conjugate states add to zero. The matrix representing μ_q in the Kramers manifold must be Hermitian since μ_q is a physically measurable quantity. So, in general, we can write

$$\bar{\bar{\mu}}_q = \begin{array}{c} \\ |\psi\rangle \\ |\theta\psi\rangle \end{array} \begin{array}{c} \begin{array}{cc} |\psi\rangle & |\theta\psi\rangle \end{array} \\ \begin{pmatrix} z_q & x_q - iy_q \\ x_q + iy_q & -z_q \end{pmatrix} \end{array} .$$

This can be written in terms of Pauli matrices as

$$\bar{\bar{\mu}}_q = x_q\bar{\bar{\sigma}}_x + y_q\bar{\bar{\sigma}}_y + z_q\bar{\bar{\sigma}}_z = \sum_j r_{(q)j}\bar{\bar{\sigma}}_j \qquad (11)$$

and we can put this in terms of a 3X3 g "matrix"

$$g_{qj} = -\frac{2}{\beta_e} r_{(q)j}$$

$$\therefore \quad \bar{\bar{\mu}}_q = -\frac{\beta_e}{2}\sum_j g_{qj}\bar{\bar{\sigma}}_j \cdot$$

The basis functions ψ and $\theta\psi$ are arbitrary in that we can choose two other states as in

$$\psi' = a\psi + b(\theta\psi)$$

$$(\theta\psi') = a^*(\theta\psi) - b^*\psi,$$

where we have used the relations in Equation (8). We can write that

$$\bar{\bar{D}} = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}, \quad \bar{\bar{\mu}}_q' = \bar{\bar{D}}\cdot\bar{\bar{\mu}}_q\cdot\bar{\bar{D}}^{-1}$$

represent the similarity-transformation matrix and μ_q' in the new basis manifold. It can be shown[65] that the change to the new matrix $\bar{\bar{\mu}}_q'$ can also be represented by a proper rotation of the vector $\vec{r}_{q(j)}$ in Equation (11). This is to say

$$\bar{\bar{\mu}}_q' = \sum_j (\bar{\bar{R}}\cdot\vec{r}_{(q)})_j\bar{\bar{\sigma}}_j = \sum_j\sum_i R_{ji}r_{(q)i}\bar{\bar{\sigma}}_j = -\frac{\beta_e}{2}\sum_j\sum_i (R^{-1})_{ij}g_{qi}\bar{\bar{\sigma}}_j \cdot$$

After changing the basis set and obtaining the new matrices $\bar{\bar{\mu}}_q'$, we can also rotate the coordinate system by the rotation matrix $\bar{\bar{S}}$ to give new $\bar{\bar{\mu}}_q''$:

$$\vec{\mu}'' = \bar{\bar{S}}\cdot\vec{\mu}', \quad \mu_r'' = \sum_q S_{rq}\mu_q'$$

$$\therefore \qquad \bar{\bar{\mu}}_r'' = \sum_q S_{rq}\bar{\bar{\mu}}_q'$$

and

$$\bar{\bar{\mu}}_r'' = -\frac{\beta_e}{2}\sum_{qji} S_{rq}g_{qi}(R^{-1})_{ij}\bar{\bar{\sigma}}_j = -\frac{\beta_e}{2}\sum_j g_{rj}''\bar{\bar{\sigma}}_j \quad ,$$

where

$$\bar{\bar{g}}'' = \bar{\bar{S}}\cdot\bar{\bar{g}}\cdot\bar{\bar{R}}^{-1} = \bar{\bar{S}}\cdot\bar{\bar{g}}\cdot\bar{\bar{R}}^{T} .$$

For the "matrix" g to be considered a second-rank (covariant) tensor, we must arbitrarily decide that for every rotation $\bar{\bar{S}}$, we will change the Kramers basis functions so that the equivalent <u>mathematical</u> rotation $\bar{\bar{R}}$ is set equal to $\bar{\bar{S}}$.

Now, if we consider the g^2 matrix formed by setting

$$\bar{\bar{G}} = \bar{\bar{g}}^T\cdot\bar{\bar{g}} \quad , \quad G_{pq} = \sum_i g_{pi}g_{qi}$$

$$\bar{\bar{G}}'' = \bar{\bar{g}}''^T\cdot\bar{\bar{g}}'' = \bar{\bar{R}}\cdot\bar{\bar{g}}^T\cdot\bar{\bar{S}}^T\cdot\bar{\bar{S}}\cdot\bar{\bar{g}}\cdot\bar{\bar{R}}^{-1} = \bar{\bar{R}}\cdot\bar{\bar{G}}\cdot\bar{\bar{R}}^{-1} . \qquad (12)$$

Using the relationships

$$(\bar{\bar{A}}\cdot\bar{\bar{B}}\cdot\bar{\bar{C}})^T = \bar{\bar{C}}^T\cdot\bar{\bar{B}}^T\cdot\bar{\bar{A}}^T \quad , \quad \bar{\bar{R}}^{-1} = \bar{\bar{R}}^T \quad , \quad \bar{\bar{S}}^{-1} = \bar{\bar{S}}^T \quad ,$$

we see that we need not put any restrictions on $\overline{\overline{G}}$, and that it is a "true" symmetric tensor.

This tensor is useful when we consider the eigenvalues of the Zeeman Hamiltonian $\mathcal{H}' = -\vec{\mu}\cdot\vec{H}$:

$$\overline{\overline{\mathcal{H}}}' = \frac{\beta_e}{2}\sum_q H_q\left(\sum_i g_{qi}\overline{\overline{\sigma}}_i\right) = \frac{\beta_e H}{2}\sum_{qi}\ell_q g_{qi}\overline{\overline{\sigma}}_i = \sum_i f_i\overline{\overline{\sigma}}_i = \begin{pmatrix} f_z & f_x-ify \\ f_x+ify & -f_z \end{pmatrix},$$

where

$$H_q = \ell_q|\vec{H}| \ , \quad f_i = \frac{\beta_e H}{q}\sum_q \ell_q g_{qi} \quad (q=x,y,z) \ ,$$

and the ℓ_q are the direction cosines of the magnetic field with respect to the original coordinate system. The eigenvalues of $\overline{\overline{\mathcal{H}}}'\vec{\xi}=E\vec{\xi}$ are obtained by setting

$$\begin{vmatrix} f_z-E & f_x-ify \\ f_x+ify & -f_z-E \end{vmatrix} = 0$$

$$E = \pm\sqrt{f_x^2+f_y^2+f_z^2} = \pm\left(\sum_i f_i^2\right)^{1/2} =$$

$$\pm\frac{\beta_e H}{2}\sum_i\left[\left(\sum_p \ell_p g_{pi}\right)\left(\sum_q \ell_q g_{qi}\right)\right]^{1/2} = \pm\frac{\beta_e H}{2}\left(\sum_{pq}\ell_p\ell_q G_{pq}\right)^{1/2}.$$

Now, when $\overline{\overline{G}}$ is diagonal, we have

$$E = \pm\frac{\beta_e H}{2}\left(\sum_p \ell_p^2 G_{pp}\right)^{1/2} = \pm g\frac{\beta_e H}{2}$$

so that a transition occurs when an incoming photon has the energy

$$\Delta E = h\nu = g\beta_e H \text{ with } g = \sqrt{\ell_x^2 g_x^2 + \ell_y^2 g_y^2 + \ell_z^2 g_z^2} \ .$$

The diagonalization of $\overline{\overline{G}}$ by the Jacobi method[66] gives the squares of the principal components (g_x^2, g_y^2, g_z^2) and the eigenvectors give the direction cosines of the new principal axes with respect to the original coordinate system.

The other mentioned interaction, $\vec{\mu}_I \cdot \vec{H}_{el}$ (Equation (10)), also lifts the degeneracy of the ground state. Following the same procedure as used for the $\overline{\overline{G}}$ tensor, we can form a pseudotensor $\overline{\overline{a}}$ and a "real" tensor $\overline{\overline{A}}$ from

$$(\overline{\overline{H}}_{el})_q = \frac{1}{2g_n\beta_n} \sum_i a_{qi} \overline{\overline{\sigma}}_i$$

$$\overline{\overline{A}} = \overline{\overline{a}}^T \cdot \overline{\overline{a}} \ , \ A_{pq} = \sum_i a_{pi} a_{qi} \ . \qquad (13)$$

Similarly, we may determine the energy levels of the perturbation $\mathcal{H}' = -\vec{\mu}_I \cdot \vec{H}_{el}$ to obtain

$$E_{\pm} = \pm \frac{|\vec{I}|A}{2} \qquad (\vec{\mu}_I = g_n\beta_n\vec{I} = \hbar\gamma_n\vec{I})$$

with

$$A = \sqrt{\ell_x^2 A_x^2 + \ell_y^2 A_y^2 + \ell_z^2 A_z^2} \ ,$$

where A_x, A_y, and A_z are the principal values of $\overline{\overline{A}}$ after it is diagonalized.

The simultaneous diagonalization of the $\overline{\overline{G}}$ and $\overline{\overline{A}}$ tensors would require that the similarity transform $\overline{\overline{R}}$ in Equation (12) diagonalize $\overline{\overline{A}}$ also or, in other words, that

one choice of coordinate axes and basis states will lead to a diagonal representation of $\overline{\overline{g}}$ and $\overline{\overline{a}}$. It has been determined[67] that, if environmental interactions are small with respect to the energy difference between the J multiplets of the species, $\overline{\overline{g}}$ and $\overline{\overline{a}}$ can be diagonalized simultaneously. This is also true for the species with rhombic symmetry, but is <u>not</u> true for those with trigonal symmetry.

Now, by using the relation

$$\vec{S} = \frac{1}{2}\sigma_x\hat{i} + \frac{1}{2}\sigma_y\hat{j} + \frac{1}{2}\sigma_z\hat{k} ,$$

we can write two terms of a spin Hamiltonian

$$\mathcal{H} = -\beta_e\vec{H}\cdot\overline{\overline{g}}\cdot\vec{S} + \vec{I}\cdot\overline{\overline{a}}\cdot\vec{S}, \qquad (14)$$

IV. <u>Isotropic Interaction</u>

The second operator in Equation (14) involves the interaction of the electrons and the nuclei. The Hamiltonian for an electron in a magnetic field can be written as

$$\mathcal{H}' = \frac{1}{2m}(\vec{P} + \frac{e\vec{A}}{c})^2 + V(\vec{r}) + g_e\beta_e\vec{H}\cdot\vec{S} ,$$

where $\vec{A}$ is the vector potential. Fermi[68] and Milford[69] have shown that the Hamiltonian has a singular part at r = 0 and a nonsingular part elsewhere. A careful evaluation of $\mathcal{H}'$ gives

$$\mathcal{H}' = \frac{g_e g_N \beta_e \beta_N \vec{I}\cdot\vec{L}}{\hbar r^3} - g_e g_N \beta_e \beta_N \left\{ \frac{\vec{I}\cdot\vec{S}}{r^3} - \frac{3(\vec{S}\cdot\vec{r})(\vec{I}\cdot\vec{r})}{r^5} \right\}' \tag{15}$$

$$+ \frac{8\pi}{3} g_e g_N \beta_e \beta_N \vec{I}\cdot\vec{S}\delta(\vec{r}) = \xi \vec{I}\cdot\vec{L} + \vec{I}\cdot\overline{\overline{D}}\cdot\vec{S} + a_{is}\vec{I}\cdot\vec{S}$$

$$= \xi \vec{I}\cdot\vec{L} + \vec{I}\cdot\overline{\overline{A}}\cdot\vec{S} \ ,$$

where $\delta(\vec{r})$ is the Dirac delta function and the prime on the second term indicates that evaluation takes place when $r \neq 0$. The second-order term $e^2A^2/2mc^2$ has been neglected since it is small under any normal experimental conditions. The third term is the Fermi contact interaction giving rise to a_{is}, the isotropic part of $\overline{\overline{a}}$. The $\delta(\vec{r})$ operator specifies the electron density at point $r = 0$ because the evaluation of $\langle \delta(\vec{r}) \rangle$ gives

$$\langle \delta(\vec{r}) \rangle = \int \psi^*(\vec{r}) \delta(\vec{r}) \psi(\vec{r}) d\tau = |\psi(0)|^2 \ .$$

The derivation of the Fermi interaction part of Equation (15) involves electromagnetic theory. It describes the energy between the nuclear magnetic moment and the magnetic field at the nucleus due to the magnetic moment of the electron. There are other interactions though, and these can give rise to non-classical results such as a negative value for a_{is}.

Consider the two structures of Figure 1,[70] where one pi electron occupies a $2p_z$ carbon orbital (which is perpendicular to the plane of three sp_2 trigonal bonds). Since the <u>spacial</u> interaction between the sigma and pi

bonds is zero, there would be no energy preference between (a) and (b). The spin interaction, however, would favor (a) and this slight polarization of the sigma bond would induce a reverse polarization of the hydrogen electron spin. Now it is this electron spin on the hydrogen atom which is interacting with the hydrogen $\vec{I}$ term. Since $\vec{S}_H = -\vec{S}_C$ for configuration (b), we have a negative interaction $\vec{I}\cdot\overleftrightarrow{a}\cdot\vec{S}$ (where $\vec{S}$ is the electron spin operator on the carbon atom), which is imputed to a negative value of a_{is}. To be more exact, we can write a more complete contact Hamiltonian, which is a function of all the electrons, as

$$\mathcal{H}_C = \frac{8\pi}{3} g_e \beta_e g_N \beta_N \sum_k \delta(\vec{r}_k - \vec{r}_N) \vec{S}_k \cdot \vec{I} \ , \qquad (16)$$

where we sum over the different electrons k, and we can define the unpaired electron density at the nucleus r_N as

$$\rho(\vec{r}_N) = \int \psi^* \sum_k 2(S_z)_k \delta(\vec{r}_k - \vec{r}_N) \psi d\tau \ ,$$

where $2(S_z)_k = +1$ or -1, depending on whether the spin is α or β, respectively; ψ is now the wave function of all the electrons k over which the summation is taken. Then we can write

$$a_{is}^{all} = \frac{4\pi}{3} g_e \beta_e g_N \beta_N \rho(\vec{r}_N)$$

$$\mathcal{H}_c = \vec{I}\cdot\overleftrightarrow{a}\cdot\vec{S}^{all} \ ,$$

where $\vec{S}^{all}$ is the complete spin operator for all the electrons summed in Equation (16).

V. Spin-Orbit Coupling

There is also an interaction between the intrinsic spin of an electron and its own angular momentum. This interaction and the angular momentum of the electron are both "caused" by the rotation of the electron about the nucleus. The general formalism that can be used to describe the interaction is that of an effective magnetic field.

The Hamiltonian in Equation (14) can be written as

$$\mathcal{H}' = \vec{B}' \cdot \vec{\mu}_e = \beta_e \vec{B}' \cdot \vec{S}$$

$$\vec{B}' = -\vec{H} \cdot \overline{\overline{g}} + \frac{1}{\beta_e} \vec{I} \cdot \overline{\overline{a}} \ , \tag{17}$$

where $\vec{B}'$ is a "real" vector, because the right-hand side of Equation (17) has the transformation properties of a vector. The revolving electron also experiences a magnetic field caused by the electric field of the nucleus which, in the electron's reference frame, is revolving in the opposite direction. The field produced is thus $\vec{B}'' = -\frac{\vec{v}}{c} \times \vec{E}$, so we have an effective magnetic field

$$\vec{B}_{eff} = \vec{B}' + \vec{B}'' = \vec{B}' - \frac{\vec{v}}{c} \times \vec{E} \ . \tag{18}$$

This will produce a torque on the intrinsic angular momentum, or the "spin" of the electron,

$$\frac{d(\hbar \vec{S})}{dt} = \vec{\mu} \times \vec{B}_{eff} \ , \tag{19}$$

where

$$\vec{\mu} = \beta_e \vec{S} = \frac{e\hbar}{mc}\vec{S} \text{ and } |\vec{S}| = \frac{1}{2} \cdot$$

It can be shown[71] that if there is an equation of the form of Equation (19), and $\vec{B}_{eff}$ is a constant with respect to time, then the particle will rotate with an angular velocity vector

$$\vec{\omega} = -(\frac{e}{mc})\vec{B}_{eff} = -\frac{e\vec{B}'}{mc} + \frac{e}{mc^2}\vec{V}\times\vec{E} \cdot \qquad (20)$$

We now can show that $\vec{B}_{eff}$ is constant. $\vec{B}'$ is constant because in Equation (17) $\vec{H}$ is the constant external magnetic field, $\vec{I}$ is constant if there are no NMR transitions, and $\overline{\overline{g}}$ and $\overline{\overline{a}}$ are parameters of the species. In considering the second part of Equation (18), we know that the electric force can be written as $e\vec{E} = -\vec{\nabla}V(r,\theta,\phi)$. We now assume that V is spherically symmetric so that

$$e\vec{E} = -\vec{\nabla}V(r) = -\frac{\vec{r}}{r}\frac{dV}{dr} , \qquad (21)$$

then

$$\vec{v}\times\vec{E} = -\frac{\vec{v}\times\vec{r}}{er}\frac{dV}{dr} = \frac{\vec{L}}{mer}\frac{dV}{dr}$$

and we know that the quantum number associated with $\vec{L}$ is constant if the electron does not change orbits. Thus, $\vec{B}_{eff}$ is constant and we obtain the result in Equation (20).

There is yet another correction to Equation (19) and this comes from special relativity theory which states

that a set of space axes that is both moving and being accelerated has, as observed from an inertial reference system, an angular velocity of precession[72, 73]

$$\vec{\omega}_T = \frac{\vec{a} \times \vec{V}}{V^2} \left[\left(1-\frac{V^2}{C^2}\right)^{-1/2} - 1\right],$$

or

$$\vec{\omega}_T = \frac{-\vec{V} \times \vec{a}}{2C^2} \text{ , when } \frac{V}{C} << 1 .$$

The coordinates of the electron have the added motion

$$\vec{\omega}_T = \frac{-\vec{V} \times (\vec{F}/m)}{2C^2} = \frac{-e}{2mc^2} \vec{V} \times \vec{E} ,$$

so that a corresponding $\vec{B}_T$ can be written with the same ratio as in Equation (20):

$$\vec{B}_T = \frac{\vec{\omega}_T}{-(e/mc)} = \frac{\vec{v} \times \vec{E}}{2c} = -\frac{1}{2}\vec{B}" .$$

This factor of one-half is called the Thomas factor. Finally, we obtain a "corrected" effective magnetic field and angular velocity,

$$\vec{B}_{corr} = \vec{B}_{eff} + \vec{B}_T = \vec{B}' - \frac{\vec{V}}{2c} \times \vec{E} ,$$

$$\vec{\omega}_{corr} = -\frac{e}{mc}\vec{B}' + \left(-\frac{e}{mc}\right)\left(-\frac{1}{2c}\right)\left(\frac{\vec{L}}{mer}\right)\frac{dV}{dr}$$

$$= -\frac{e}{mc}\vec{B}' + \frac{1}{2mc^2}\vec{L}\,\frac{1}{r}\,\frac{dV}{dr}$$

by using Equations (20) and (21). The magnetic interaction is

$$\mathcal{H}' = \vec{B}_{corr}\cdot\vec{\mu} = \frac{e\hbar}{mc}\vec{B}_{corr}\cdot\vec{S} = \hbar\,\vec{\omega}_{corr}\cdot S$$

$$= -\frac{e\hbar}{mc}\vec{B}'\cdot\vec{S} + \frac{\hbar}{2mc^2}\vec{L}\cdot\vec{S}\,\frac{1}{r}\frac{dV}{dr}$$

$$= \frac{e\hbar}{mc}\vec{H}\cdot\overline{\overline{g}}\cdot\vec{S} + \vec{I}\cdot\overline{\overline{a}}\cdot\vec{S} + \frac{\hbar}{2mc^2}\vec{L}\cdot\vec{S}\,\frac{1}{r}\frac{dV}{dr}$$

$$\therefore \quad \mathcal{H}' = \beta_e\vec{H}\cdot\overline{\overline{g}}\cdot\vec{S} + \vec{I}\cdot\overline{\overline{a}}\cdot\vec{S} + \lambda\vec{L}\cdot\vec{S}\ ,$$

where $\lambda = \frac{\hbar}{2mc^2}\frac{1}{r}\frac{dV}{dr}$;

λ is the spin-orbit coupling constant.

VI. Spin-Spin Coupling

There is a tensor form of coupling between any nuclear spins $\vec{I}_i$ and $\vec{I}_j$,

$$\mathcal{H}_D = g_N^2\beta_N^2\,\vec{I}_i\cdot\overline{\overline{D}}_I\cdot\vec{I}_j$$

which is derived in the same way as the second term in Equation (15). This is caused by the interaction of the dipole moments of the nuclei. The effect of this term in liquids is proportional to the trace of $\overline{\overline{D}}_I$. A simple evaluation in any coordinate system shows the trace to be zero.[74]

There can also be an isotropic term

$$\mathcal{H}_D = J_{ij}\vec{I}_i\cdot\vec{I}_j\ ,$$

where J_{ij} is an interaction not completely understood. One important interaction mechanism is the correlation of

nuclear spins through the polarization of the intervening electron spins,[75] which is analogous to the mechanism described above concerning Figure 1.

VII. Orbital Angular Momentum

There is also a classical energy term $E = -\vec{H}\cdot\vec{L}$, where $\vec{L}$ is the orbital angular momentum of the electron. This is a first-order approximation, in contrast to the exact energy of $-\vec{H}\cdot\vec{I}$, because the former case does not consist of an infinitesimally localized current distribution as is postulated for the "spin."[76] The higher-order terms are neglected though, and we have the added quantum mechanical analogue

$$\mathcal{H}' = \vec{H}\cdot\vec{L}_{\text{operator}} .$$

This term sometimes does not contribute much to the expectation value of the Hamiltonian, or in other words, to the energy of the system.[77] This is because we can evaluate $\langle L_z \rangle$ as

$$\langle L_z \rangle = \langle \psi | -i\hbar \frac{\partial}{\partial \phi} | \psi \rangle = -i\hbar \int \psi^* \frac{\partial}{\partial \phi} \psi \, d\tau$$

and, if $\psi = \psi^*$, then

$$\langle L_z \rangle = -i\hbar \int \frac{1}{2} \frac{\partial}{\partial \phi} (\psi^* \psi) \, d\tau = iK .$$

Now K=0 because the expectation value must be real. So, whenever the wavefunction for the system can be chosen to be real, we have $\langle L_z \rangle = 0$. This can always be done in

non-degenerate systems by multiplying by an appropriate phase factor, which is always allowed.

Species which do not have orbitally degenerate ground states would then have a "quenched" orbital angular momentum interaction. This would also be true for the radicals studied in this work since the Kramers degeneracy is lifted by the magnetic field.

VIII. Nuclear g Tensor

The Hamiltonian can include a nuclear term[78]

$$\mathcal{H}_N = -\beta \vec{H} \cdot \overline{\overline{g}}^{(I)} \cdot \vec{I}$$

similar to that of the electron in the first term of Equation (14). The tensor quality would come about by changes in the magnetic field felt by the nucleus that were caused by changes in the electron wave function. The distortion of the electronic cloud can be caused by, and be approximately proportional to, the external magnetic field H. This is not important in our studies.

IX. Electric Quadrupole Coupling

There is also a nuclear electric quadrupole coupling. This comes about when the interaction energy of a charge distribution and an electric potential V due to external sources is expanded about the origin:[79]

$$\text{Energy} = q\Phi(0) - \vec{p} \cdot \vec{E}(0) - \frac{1}{6} \sum_{ij} Q_{ij} V_{ij} + \ldots ,$$

where

$$Q_{ij} = \int (3x_i x_j - \delta_{ij} r^2) \rho \, d\tau$$

$$V_{ij} = \frac{\partial E_j(0)}{\partial x_i} \quad .$$

By using the Wigner-Eckart theorem,[80] it can be shown that the quadrupole term can be changed from an expression involving integration over coordinates to an equivalent form in I_x, I_y, and I_z by multiplying the former by a constant. This changes the form to

$$\mathcal{H}_Q = \frac{eQ}{6I(2I-1)} \sum_{ij} V_{ij} [\tfrac{3}{2}(I_i I_j + I_j I_i) - \delta_{ij} I^2] = \vec{I} \cdot \overline{\overline{P}} \cdot \vec{I} \, .$$

From the properties of second-order partial derivatives, we have $V_{ij}=V_{ji}$ which implies $P_{ij}=P_{ji}$. Then the symmetric real matrix $\overline{\overline{P}}$ can be diagonalized by choosing a new set of axes to give the form[81]

$$\mathcal{H}_Q = P_x I_x^2 + P_y I_y^2 + P_z I_z^2$$

$$= K + P_{\parallel} \left[\{ I_z^2 - \tfrac{1}{3} I(I+1) \} + \frac{1}{6} \eta \, (I_+^2 - I_-^2) \right] ,$$

where

$$K = \tfrac{1}{2}(I_x + I_y + I_z)[I(I+1) - I_z^2]$$

$$P_{\parallel} = \tfrac{3}{2} I_z = \frac{3eQq}{4I(2I-1)} \qquad q = \frac{\partial^2 V}{\partial z^2}$$

$$\eta = (I_x - I_y)/I_z \qquad I_{\pm} = I_x \pm i I_y$$

and we have K=0 because the Laplace equation $\nabla^2 V = \sum_i V_{ii} = 0$ implies $P_x + P_y + P_z = 0$.

We see that the η term is a second-order effect compared to the other term in brackets, and when axial symmetry is present, $\eta = 0$.

X. Spin Hamiltonians

The energy transitions observed in any type of magnetic resonance experiment can generally be described in terms of an appropriate spin Hamiltonian. The Schroedinger equation to be solved is generally very complicated. The various terms of a general spin Hamiltonian can be re-written in terms of raising and lowering operators to give expressions which are in a form suitable for a computer.[82] Approximate formulas for the energy have been obtained from some Hamiltonians by specifying simplifying conditions and using first- and second-order perturbation theory.

We list below some of the spin Hamiltonians and various formulas that have been derived. In the perturbation cases, it is assumed that the first term has a much greater contribution to the energy than the rest.

Let M be the quantum state of $\vec{S}$,

Let m be the quantum state of $\vec{I}$,

Let W be the energy of a quantum state,

Let $h\nu$ be the energy needed for an $(M-1) \leftrightarrow (M)$ transition.

A. Electron Zeeman Hamiltonian

$$\mathcal{H} = \beta \vec{H} \cdot \overline{\overline{g}} \cdot \vec{S}$$

Condition: $\vec{H}$ has direction cosines (ℓ_x, ℓ_y, ℓ_z) with respect to the principal axes of $\overline{\overline{g}}$: $(\vec{g}_x, \vec{g}_y, \vec{g}_z)$.

The exact solution is[82, 83]

$$W = g\beta HM$$

$$h\nu = g\beta H \ ,$$

where

(1) if $\overline{\overline{g}}$ has different principal values,

$$g = \sqrt{g_x^2 \ell_x^2 + g_y^2 \ell_y^2 + g_z^2 \ell_z^2} \qquad (22)$$

(2) if $\overline{\overline{g}}$ is axially symmetric, i.e., $g_x = g_y = g_{\parallel}$, $g_z = g_{\perp}$, and $\vec{H}$ makes an angle θ with $\vec{g}_{\parallel}$,

$$g = \sqrt{g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta} \ . \qquad (23)$$

B. Hamiltonian A Plus Hyperfine Interaction

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

Conditions: $\vec{H}$ has direction cosines (ℓ_x, ℓ_y, ℓ_z) with respect to the principal axes of $\overline{\overline{g}}$. These axes define the coordinate system.

(1) The First-Order Approximation:

$$\begin{aligned} W &= g\beta HM + AmM \\ h\nu &= g\beta H + Am \ , \end{aligned} \qquad (24)$$

where

(a) if $\overline{\overline{g}}$ and $\overline{\overline{A}}$ have different principal axes,[84]

$$A = \{(\ell_x g_x A_{xx} + \ell_y g_y A_{yx} + \ell_z g_z A_{zx})^2 + (\ell_x g_x A_{xy} + \ell_y g_y A_{yy} + \ell_z g_z A_{zy})^2 + (\ell_x g_x A_{xz} + \ell_y g_y A_{yz} + \ell_z g_z A_{zz})^2\}^{1/2}/g \ , \quad (25)$$

and g is given by Equation (22);

(b) if $\overline{\overline{g}}$ and $\overline{\overline{A}}$ have the same principal axes,

$$A = \{\ell_x^2 g_x^2 A_x^2 + \ell_y^2 g_y^2 A_y^2 + \ell_z^2 g_z^2 A_z^2\}^{1/2}/g, \quad (26)$$

with g given by Equation (22);

(c) if $\overline{\overline{g}}$ and $\overline{\overline{A}}$ have the same principal axes, and are axially symmetric with $\vec{H}$ making an angle θ with $\vec{g}_{\parallel}$,

$$A = \{g_{\parallel}^2 A_{\parallel}^2 \cos^2\theta + g_{\perp}^2 A_{\perp}^2 \sin^2\theta\}^{1/2}/g \quad (27)$$

with g given by Equation (23).

(2) The Second-Order Approximation[85]

(a) If $\overline{\overline{g}}$ and $\overline{\overline{A}}$ have the same principal axes, and the direction of H is described in this principal-axis coordinate system by the standard polar angles θ and ϕ,

$$W = g\beta HM + AmM - \frac{A_xA_yA_z}{2g\beta HA}\,[S(S+1)-M^2]m + ZM$$

$$h\nu = g\beta H + Am + \frac{A_xA_yA_z}{2g\beta HA}\,[2M+1]m + Z\,,$$

where

$$Z = \{\frac{g_z^2(g^2A_p^2-g_p^2A_z^2)^2}{g_p^2g^4A^2}\cos^2\theta + \frac{g_x^2g_y^2(A_x^2-A_y^2)^2}{g_p^2g^2A^2}\sin^2\phi\cos^2\phi\}\frac{m^2\sin^2\theta}{2g\beta H}$$

$$+ \{\frac{g^2A_p^2A_z^2}{g_p^2A^2} + \frac{g_p^2A_x^2A_y^2}{g^2A_p^2}$$

$$+ \frac{g_x^2g_y^2g_z^2A_z^2(A_x^2-A_y^2)^2}{g_p^2g^4A^2A_p^2}\cos^2\theta\sin^2\phi\cos^2\phi\}\,\frac{[I(I+1)-m^2]}{4g\beta H}$$

$$A = (g^2A_p^2\sin^2\theta + g_z^2A_z^2\cos^2\theta)^{1/2}/g,$$

$$A_p = (g_x^2A_x^2\cos^2\phi + g_y^2A_y^2\sin^2\phi)^{1/2}/g$$

$$g = (g_p^2\sin^2\theta + g_z^2\cos^2\theta)^{1/2}\,,\ g_p = (g_x^2\cos^2\phi + g_y^2\sin^2\phi)^{1/2}.$$

(b) if $\overline{\overline{g}}$ and $\overline{\overline{A}}$ have the same principal axes, and are axially symmetric with $\vec{H}$ making an angle θ with $\vec{g}_{\parallel}$,

$$W = g\beta HM + T_A$$

$$h\nu = g\beta H + U_A\,,$$

where

$$T_A = ZM - \frac{A_\perp^2 A_\parallel}{2g\beta HA}\,[S(S+1)-M^2]m \tag{28}$$

$$U_A = Z + \frac{A_\perp^2 A_\parallel}{2g\beta HA}\,[2M+1]m, \tag{29}$$

$$Z = \frac{g_\parallel^2\, g_\perp^2 (A_\parallel^2 - A_\perp^2)^2}{2g^5\beta HA^2}\, m^2\sin^2\theta\cos^2\theta + \frac{A_\perp^2(A_\perp^2 + A_\parallel^2)}{4g\beta HA^2}\,[I(I+1)-m^2]$$

and g and A are given by Equations (23) and (27), respectively.

C. Hamiltonian B plus Zero-Field Splitting

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

Conditions: $\overline{\overline{g}}, \overline{\overline{A}}, \overline{\overline{D}}$ have different principal axes. $\vec{H}$ has direction cosines (ℓ_x, ℓ_y, ℓ_z) with respect to any arbitrary coordinate system (x,y,z). $\overline{\overline{g}}, \overline{\overline{A}}$, and $\overline{\overline{D}}$ are expressed in this coordinate system.

The second-order approximation is[86]

$$h\nu = g\beta H + AM + \frac{1}{2g\beta H}\,(T_{xx}T_{yy} - T_{xy}T_{yx})(2M+1)m$$

$$+ \frac{T_{xx}^2 + T_{yy}^2 + T_{xy}^2 + T_{yx}^2}{4g\beta H}\,[I(I+1)-m^2] + \frac{T_{xz}^2 + T_{yz}^2}{2g\beta H}\,m^2$$

$$- \frac{D_{xz}'^2 + D_{yz}'^2}{2g\beta H}\,[4S(S+1)-24M(M+1)-9]$$

$$+ \frac{(D_{xx}' - D_{yy}')^2 + 4D_{xy}'^2}{8g\beta H}\,[2S(S+1)-6M(M+1)-3]\ ,$$

where

$$T_{ij} = \sum_{mn} U_{mi} V_{nj} A_{mn}$$

$$D'_{ij} = \sum_{mn} U_{mi} U_{nj} D_{mn}$$

$$A = \left(\sum_{ijk} K_i K_j A_{ik} A_{jk} \right)^{1/2} / g$$

$$g = \left(\sum_{ijk} \ell_i \ell_j g_{ik} g_{jk} \right)^{1/2}, \quad K_n = \sum_m \ell_m g_{mn}$$

$$\overline{\overline{U}} = \begin{pmatrix} K_2/Y & K_1K_3/gY & K_1/g \\ -K_1/Y & K_2K_3/gY & K_2/g \\ 0 & -Y/g & K_3/g \end{pmatrix}$$

$$Y = \sqrt{K_1^2 + K_2^2} \, .$$

$\overline{\overline{V}}$ is obtained from $\overline{\overline{U}}$ by changing K_i to $K'_i = \sum_j K_j A_{ji}$ and g to Ag.

D. Hamiltonian C plus Electric Quadrupole and Nuclear Zeeman Terms

$$\mathcal{H} = \beta \vec{H} \cdot \overline{\overline{g}} \cdot \vec{S} + \vec{I} \cdot \overline{\overline{A}} \cdot \vec{S} + \vec{S} \cdot \overline{\overline{D}} \cdot \vec{S} + \vec{I} \cdot \overline{\overline{P}} \cdot \vec{I} - \beta \vec{H} \cdot \overline{\overline{g}}^{(I)} \cdot \vec{I}$$

Conditions: $\overline{\overline{g}}, \overline{\overline{A}}, \overline{\overline{D}}, \overline{\overline{P}}$, and $\overline{\overline{g}}^{(I)}$ have the same principal axes. $\vec{H}$ has direction cosines (ℓ_x, ℓ_y, ℓ_z) with respect to the principal axes of $\overline{\overline{g}}$, which define the coordinate system.[87]

(1) The First-Order Approximation:

$$W = g\beta HM + AmM + D''(M-\tfrac{1}{2}) + P\{m^2-\tfrac{1}{3}I(I+1)\} - G_I m$$

$$h\nu = g\beta H + Am + D'' ,$$

where g and A are given by Equations (22) and (26), respectively, and

$$D'' = 3(\ell_x^2 g_x^2 D_x + \ell_y^2 g_y^2 D_y + \ell_z^2 g_z^2 D_z)/g^2$$

$$P = \tfrac{3}{2}(\ell_x^2 g_x^2 A_x^2 P_x + \ell_y^2 g_y^2 A_y^2 P_y + \ell_z^2 g_z^2 A_z^2 P_z)/g^2A^2$$

$$G_I = \beta H(\ell_x^2 g_x A_x g_x^{(I)} + \ell_y^2 g_y A_y g_y^{(I)} + \ell_z^2 g_z A_z g_z^{(I)})/gA .$$

(2) If we also have axial symmetry for all the tensors, we have the Second-Order Approximation:

$$W = g\beta HM + T_A + T_D + T_P + T_g$$

$$h\nu = g\beta H + U_A + U_D + U_P ,$$

where T_A, U_A correspond only to the $\vec{I}\cdot\overline{\overline{A}}\cdot\vec{S}$ term,

T_D, U_D correspond only to the $\vec{S}\cdot\overline{\overline{D}}\cdot\vec{S}$ term,

T_P, U_P correspond only to the $\vec{I}\cdot\overline{\overline{P}}\cdot\vec{I}$ term,

T_g corresponds only to the $-\beta\vec{H}\cdot\overline{\overline{g}}^{(I)}\cdot\vec{I}$ term,

so that any Hamiltonian made up of only some of the tensors has only those corresponding terms in the equations for W and hν.

T_A and U_A are given by Equations (28) and (29), respectively.

$$T_D = \tfrac{1}{2}D\{(3g_{\|}^2/g^2)\cos^2\theta-1\}\{M^2-\tfrac{1}{3}S(S+1)\}$$

$$+ (g_{\|}^2\, g_{\perp}^2/g^4)(D^2\cos^2\theta\sin^2\theta/2X)M\{8M^2+1-4S(S+1)\}$$

$$+ (g_{\perp}^4/g^4)(D^2\sin^4\theta/8X)M\{2S(S+1)-2M^2-1\}$$

$$U_D = D\{2g_{\|}^2\cos^2\theta-g_{\perp}^2\sin^2\theta\}/g^2$$

$$+ (g_{\|}^2\, g_{\perp}^2/g^4)(D^2\cos^2\theta\sin^2\theta/2X)\{24M(M-1)+9-4S(S+1)\}$$

$$+ (g_{\perp}^4/g^4)(D^2\sin^4\theta/8X)\{2S(S+1)-6M(M-1)-3\}$$

$$T_P = P\{m^2-\tfrac{1}{3}I(I+1)\} + \left(\frac{g_{\|}\, g_{\perp} A_{\|}\, A_{\perp}}{g^2A^2}\right)^2\{P_{\|}^2\sin^2 2\theta/8AM\}m$$

$$\{8m^2+1-4I(I+1)\}$$

$$+ (g_{\perp}A_{\perp}/gA)^4\{P_{\|}^2\sin^4\theta/8AM\}m\{2I(I+1)-2m^2-1\}$$

$$U_P = -(g_{\|}\, g_{\perp}A_{\|}\, A_{\perp}/g^2A^2)^2\{P_{\|}^2\sin^2 2\theta/8AM(M-1)\}m\{8m^2+1-4I(I+1)\}$$

$$- (g_{\perp}A_{\perp}/gA)^4\{P_{\|}^2\sin^4\theta/8AM(M-1)\}m\{2I(I+1)-2m^2-1\}$$

$$T_g = -(\beta Hm/gA)(g_{\|}^{(I)}g_{\|}\, A_{\|}\cos^2\theta + g_{\perp}^{(I)}g_{\perp}A_{\perp}\sin^2\theta)$$

$$D = \tfrac{3}{2}\, D_{\|}$$

$$X = g\beta H$$

$$P = \tfrac{3}{2}\{g_{\|}^2\, A_{\|}^2\, P_{\|}\cos^2\theta + g_{\perp}^2A_{\perp}^2P_{\perp}\sin^2\theta\}/g^2A^2\ .$$

g and A are given by Equations (23) and (27), respectively.

XI. Determination of ESR Parameters

In general, the parameters of the $\bar{\bar{g}}$ and $\bar{\bar{A}}$ tensors are determined from isofrequency plots, where the frequency ν is constant and H is swept through a range for each of several orientations of a crystal rotated about a specific axis. To determine the values of the magnetic field at which resonance occurs, we can use Equation (24) for a first-order approximation:

$$H = \frac{h\nu}{g\beta} - \sum_p m_p \left(\frac{A_p}{g\beta}\right) = H_0 - \sum_p m_p A_p' ,$$

where A_p is the hyperfine interaction with the p^{th} nucleus and has appropriate energy related units (usually MHz), A_p' corresponds to A_p but has units of gauss, and m_p is the quantum number of the p^{th} nucleus with values from $-I_p$ to $+I_p$. Halfway between the outer lines of any hyperfine multiplet would be the place where (perhaps only mathematically) $m_p = 0$. Choosing the midpoint between the outermost lines of the whole spectrum will give $H_0 = h\nu/g\beta$. By considering only these midpoints, we have a "reciprocal g-value" plot for the crystal. The values of A_p are determined by measuring the distance between the outer lines of the corresponding multiplet and dividing by $2I_p$. By plotting these values versus the angle of

rotation of the crystal, we obtain A-value plots. We thus have two symmetric covariant second-rank tensors to determine.

Since g is given by Equation (22), it can be rewritten as

$$g^2 = \sum_i \ell_i^2 g_i^2 \, .$$

If we form the symmetric diagonalized g tensor as

$$G'_{ij} = g_i \delta_{ij} = G'_{ji} \, , \tag{30}$$

where δ_{ij} is the Kronecker delta function, then we can write

$$g^2 = \sum_i \ell_i^2 \sum_j g_i \delta_{ij} g_i \delta_{ij} = \sum_i \ell_i^2 \sum_j G'_{ij} G'_{ji}$$

$$= \sum_i \ell_i^2 (\overline{\overline{G}}' \cdot \overline{\overline{G}}')_{ii} = \sum_i \ell_i^2 (\overline{\overline{R}}^{-1} \cdot \overline{\overline{R}}\ \overline{\overline{G}}' \cdot \overline{\overline{R}}^{-1} \cdot \overline{\overline{R}} \cdot \overline{\overline{G}}' \cdot \overline{\overline{R}}^{-1} \cdot \overline{\overline{R}})_{ii}$$

$$= \sum_{imn} \ell_i^2 R_{im}^{-1} [(\overline{\overline{R}} \cdot \overline{\overline{G}}' \cdot \overline{\overline{R}}^{-1}) \cdot (\overline{\overline{R}} \cdot \overline{\overline{G}}' \cdot \overline{\overline{R}}^{-1})]_{mn} R_{ni}$$

$$= \sum_{imn} (R_{mi} \ell_i)(R_{ni} \ell_i)(\overline{\overline{G}} \cdot \overline{\overline{G}})_{mn}$$

$$\therefore \quad g^2 = \sum_{mn} \ell'_m \ell'_n W_{mn} , \tag{31}$$

where

$$\overline{\overline{W}} = \overline{\overline{G}}^2 \ , \ \overline{\overline{R}}^{-1} = \overline{\overline{R}}^T \, . \tag{32}$$

Here $\overline{\overline{R}}$ is an orthogonal matrix which represents a proper rotation to a new coordinate system, and ℓ_m' and $\overline{\overline{G}}'$ are the direction cosines of $\vec{H}$ and the new representation of $\overline{\overline{G}}$ in this new coordinate system, respectively. Equation (31) is of the same form as Equation (4) in Part II of this thesis, so the values of the W matrix can be determined by any of the methods presented there.

To solve for $\overline{\overline{G}}$, we can first diagonalize $\overline{\overline{W}}$ by a similarity transformation

$$\overline{\overline{S}}\cdot\overline{\overline{W}}\cdot\overline{\overline{S}}^T = \overline{\overline{W}}' \text{(diagonalized)} \cdot \tag{33}$$

Then, by forming a diagonal matrix whose diagonal elements are the square roots of the corresponding ones in W', one obtains

$$\overline{\overline{G}}'\cdot\overline{\overline{G}}' = \overline{\overline{W}}' , \tag{34}$$

but, from Equation (33), we have

$$\overline{\overline{W}} = \overline{\overline{S}}^T\cdot\overline{\overline{W}}'\cdot\overline{\overline{S}}$$

$$\overline{\overline{W}} = (\overline{\overline{S}}^T\cdot\overline{\overline{G}}'\cdot\overline{\overline{S}})\cdot(\overline{\overline{S}}^T\cdot\overline{\overline{G}}'\cdot\overline{\overline{S}}) = \overline{\overline{G}}\cdot\overline{\overline{G}} ,$$

so $\overline{\overline{G}} = \overline{\overline{S}}^T\cdot\overline{\overline{G}}'\cdot\overline{\overline{S}}$ is the solution to Equation (32).

We now want to determine $\overline{\overline{A}}$ for the most general case in which $\overline{\overline{g}}$ and $\overline{\overline{A}}$ have different principal axes. If we multiply the terms out and rearrange them in Equation (25), and use primes to signify the fact that the $\overline{\overline{g}}$ and $\overline{\overline{A}}$ terms are in the $\overline{\overline{g}}$ principal-value coordinate system, we get

$$g^2A^2 = \sum_{ij} X'_{ij} \ell'_i \ell'_j \quad , \quad (i,j = x,y,z)$$

where a typical term is

$$X'_{ij} = g_i g_j (A'_{ix}A'_{jx} + A'_{iy}A'_{jy} + A'_{iz}A'_{jz})$$

$$= g_i g_j \sum_k A'_{ik}A'_{jk} \quad .$$

Using Equation (30) and the fact that $\bar{\bar{A}}$ is symmetric from Equation (13), we can write

$$g^2A^2 = \sum_{ij} (g_i A'_{ik})(g_j A'_{jk}) \ell'_i \ell'_j$$

$$= \sum_{kij} (\sum_l g_i \delta_{il} A'_{lk})(\sum_m g_m \delta_{mj} A'_{mk}) \ell'_i \ell'_j$$

$$= \sum_{kij} (\sum_l G'_{il} A'_{lk})(\sum_m A'_{km} G'_{mj}) \ell'_i \ell'_j$$

$$= \sum_{kij} (\bar{\bar{G}}' \cdot \bar{\bar{A}}')_{ik} (\bar{\bar{A}}' \cdot \bar{\bar{G}}')_{kj} \ell'_i \ell'_j$$

$$= \sum_{ij} (\bar{\bar{G}}' \cdot \bar{\bar{A}}' \cdot \bar{\bar{A}}' \cdot \bar{\bar{G}}')_{ij} \ell'_i \ell'_j$$

$$\therefore \quad g^2A^2 = \sum_{ij} X'_{ij} \ell'_i \ell'_j \quad ,$$

where

$$\bar{\bar{X}}' = \bar{\bar{G}}' \cdot \bar{\bar{A}}' \cdot \bar{\bar{A}}' \cdot \bar{\bar{G}}' \quad .$$

Hence, in any coordinate system, we can write

$$g^2A^2 = \sum_{ij} X_{ij}\ell_i\ell_j$$

$$\overline{\overline{X}} = \overline{\overline{G}}\cdot\overline{\overline{A}}\cdot\overline{\overline{A}}\cdot\overline{\overline{G}} \ ,$$

which again is of the same form as Equation (4) of Part II. We can solve for $\overline{\overline{A}}$ by determining $\overline{\overline{X}}$ from angular variation of the quantity g^2A^2 by any procedure in Part II, then solving the equation

$$\overline{\overline{A}}\cdot\overline{\overline{A}} = \overline{\overline{G}}^{-1}\cdot\overline{\overline{X}}\cdot\overline{\overline{G}}^{-1}$$

by the method mentioned for Equation (34). This result has been stated elsewhere.[88] If $\overline{\overline{g}}$ and $\overline{\overline{A}}$ have the same principal axes, then the principal values of $\overline{\overline{A}}$ are found by diagonalizing $\overline{\overline{X}}$ to give $\overline{\overline{X}}'$ and using the equation

$$A'_{ii} = \sqrt{X'_{ii}}/G'_{ii} \ .$$

If the relative anisotropy of g is much smaller than that of A, we can treat A exactly as we did g, that is

if
$$\left(\frac{\Delta g}{g_{iso}}\right) \ll \left(\frac{\Delta A}{A_{iso}}\right) \qquad (35)$$

then

$$A = \sqrt{\ell_x^2A_x^2 + \ell_y^2A_y^2 + \ell_z^2A_z^2}$$

$$\therefore \quad A^2 = \sum_{mn} \ell_m\ell_nW_{mn} \ ,$$

where $\overline{\overline{W}} = \overline{\overline{A}} \cdot \overline{\overline{A}}$

Δg is the largest anisotropy of $\overline{\overline{g}}$

ΔA is the largest anisotropy of $\overline{\overline{A}}$

g_{iso} is the isotropic value of $\overline{\overline{g}}$

A_{iso} is the isotropic value of $\overline{\overline{A}}$.

EXPERIMENTAL

I. Spectrometers

Three ESR spectrometers were used, two of them X-band systems and one a Q-band system. The X-band systems were used with a magnetic field of about 3300 gauss and a resonant frequency of about 9.5 GHz. while the Q-band system was used with the corresponding values 12000 gauss and 35 GHz., respectively.

One spectrometer was the Varian V-4502 X-band system with a 12-inch magnet and 100 KHz. modulation. First- or second-derivative spectra were taken on various XY-recorders. The appropriate derivative of the absorption mode was plotted as a function of the magnetic field intensity. The magnetic field was measured by accurately determining the proton NMR resonance frequency of a water sample and using the equation [89]

$$H(\text{gauss}) = 0.2348682\ \nu_{\text{water}}(\text{MHz}).$$

A homemade marginal oscillator[90] was used to detect the proton resonance and the frequency was measured with a Hewlett-Packard Model 524C electronic counter. After each spectrum was taken on the XY-recorder, two accurate

magnetic field determinations were made on top of the spectrum. From this, it was found that the linearity of the magnetic field sweep and the stability of the absolute magnetic field on the spectra were within the experimental error of the NMR probe measurements. The klystron frequency was measured using a TS-148/UP U.S. Navy spectrum analyzer with a calibration chart; the accuracy was about 1 part in 10^5.

For some preliminary spectra, a Varian E-4 X-band spectrometer was used. This also had 100 KHz. modulation, but the magnet had 4-inch diameter pole pieces. The absolute magnetic field, the magnetic field sweep, and the klystron frequency were read from the dials on the machine.

The Q-band spectrometer was a Varian V-4503 system with a 12-inch magnet and 100 KHz. modulation. There was no external probe to measure the magnetic field accurately. The klystron frequency was determined by the wavemeter of the Varian V-4561 35 GHz. Microwave Bridge. Repeated measurements indicated that the stability of the klystron frequency was only 1 part in 10^4.

The X-band spectrometers had provisions for keeping samples immersed in liquid nitrogen and all three spectrometers could be used with a Varian V-4540 variable temperature controller. This instrument regulates the sample temperature by passing over it a stream of gaseous nitrogen whose temperature is controlled by either being passed

through a helical tube immersed in liquid nitrogen and/or warmed by heating filaments.

A common sequence of measurements involves mounting an irradiated crystal with a chosen axis vertical. When the X-band system was used, magnetic field sweeps were made with the crystal progressively rotated about that axis. With the Q-band system, the magnetic field was instead rotated about the sample. This is the more desirable arrangement since moving the crystal in the cavity changes the Q of the system which tends to change the klystron frequency and the detector current leakage. The magnet on the V-4502 was not rotated because the connecting hoses were too short.

II. Crystal Irradiation and Mounting

There are two methods for mounting crystals that must be kept at liquid nitrogen temperature. One method is to irradiate the crystal, then mount it between flexible brass strips. This method, which is described in the thesis by Watson,[60] has problems associated with it. It is difficult to align and ascertain the alignment of the crystal. The lack of space caused by the presence of the brass strips in the liquid nitrogen Dewar makes liquid nitrogen bubbling more likely because of "hot spots" on sharp edges of the brass. Also, any bubbling that occurs tends to shake the crystal causing electronic stability problems and creates a possibility of accidental realignment

of the crystal. The metal in the cavity also lowers the sensitivity of the instrument.

Another method is first to glue the crystal (Pliobond cement, Goodyear Rubber Co., Akron, Ohio) onto a copper wire which in turn is imbedded into a thin glass rod. This allows one to adjust accurately the axis of rotation. The whole assembly is then irradiated and used in the same way as the crystal holder in the first method. An extra signal at g = 2.0026 is introduced from the irradiated glue.

There were two sources of irradiation used. One was a ^{60}Co γ-ray source that had an intensity of 1.0×10^6 rad/hr. The other was a 1 Mev electron source (G.E. XRD-1 Resonant Transformer) that had a dose rate of 1.8×10^7 rad/hr.

III. ENDOR Measurements

Some electron-nuclear double-resonance (ENDOR) measurements were made on crystals of dl-mandelic acid. A Varian E-700 ENDOR system was used with the V-4502 X-band spectrometer. A Monsanto Model 1100A counter-timer was used to determine the rf pulse frequencies.

IV. X-ray Crystallography

dl-Mandelic acid, $C_6H_6CHOHCOOH$, in powdered form was obtained from Matheson Coleman and Bell Co. Crystals were grown from saturated aqueous solutions by slow

evaporation. The morphology of the crystals was the same as determined by Rose.[91] He reported that the crystal system was orthorhombic with cell dimensions a = 9.66± 0.05 Å, b = 16.20 ± 0.08 Å, and c = 9.94 ± 0.05 Å, and that the number of molecules per unit cell was eight. An orthographic projection of dl-mandelic acid is shown in Figure 2. Small crystals of about 0.1 mm. length were grown in a shallow dish by slow evaporation from water. The crystal chosen had a clear-cut morphology that allowed us to mount it specifically about the a axis. This was confirmed by taking oscillation photographs[92] using a Weissenberg Camera (Supper Co., Watertown, Mass.) with filtered Cu ($\lambda_{K\alpha}$ = 1.5418 Å) radiation. The cell dimensions were determined from these photographs and compared with those reported by Rose.[91] There was excellent agreement within experimental error. The oscillation photographs were used also to align the rotation axis of the crystal accurately along the a axis. The zero-, first-, and second-layer photographs were taken about the a axis. By considering the symmetry of the missing reflections, we were able to determine the limiting conditions for reflection in terms of the hkl indices. This uniquely determined the space group out of the 74 possible ones for the orthorhombic case.

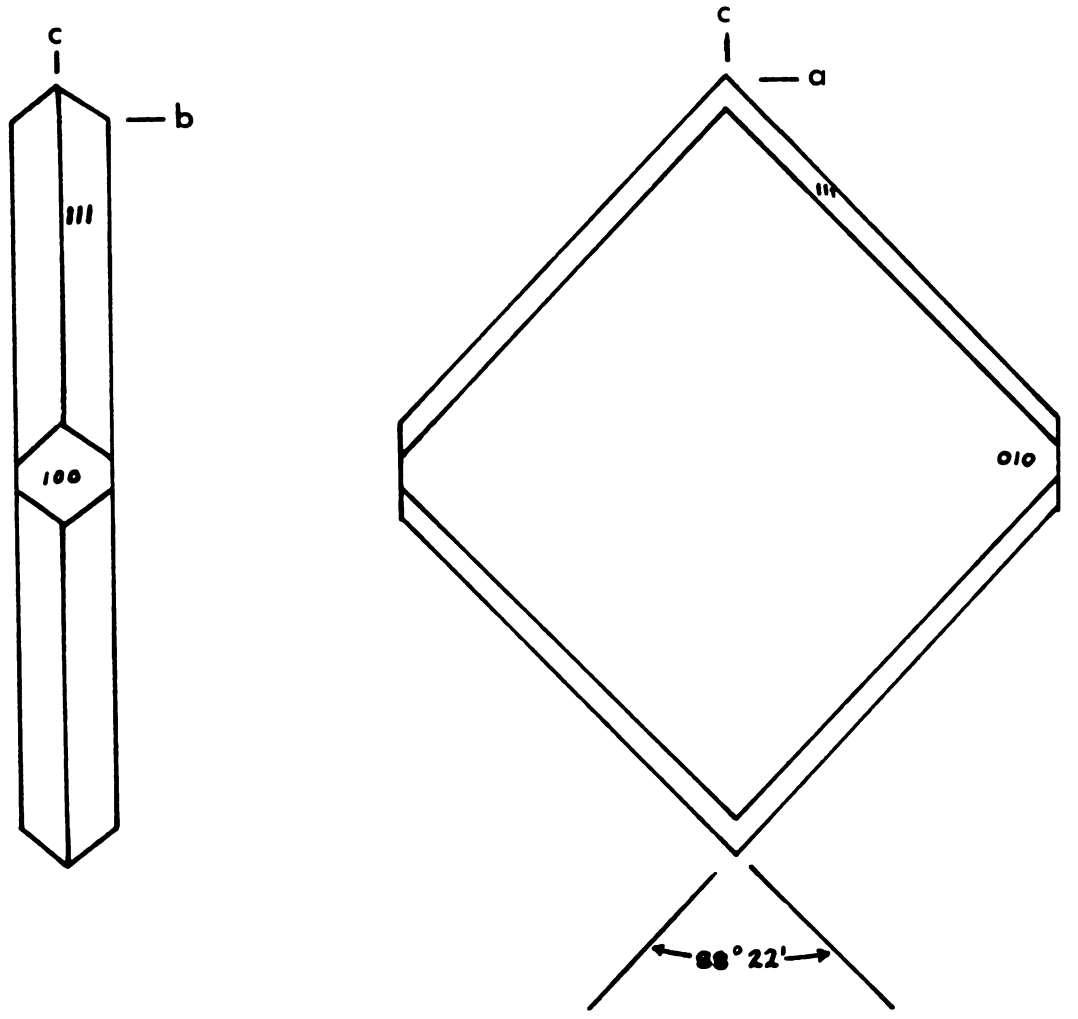


Figure 2. Orthographic projection of a crystal of dl-mandelic acid.

V. Parameters From Tensor Variations

The purpose of this section is to describe a way in which the $\bar{\bar{g}}$ and $\bar{\bar{A}}$ tensor parameters can be determined when there is restricted information from the isofrequency plots. This was the case for mandelic acid when the normal analysis utilizing Schonland's method[93] did not work. The reason that Schonland's method, and the method outlined in Part II for the orthogonal case, both tend to have difficulty is because they depend heavily on the high accuracy of the g-values for all three rotations. This is difficult to achieve since three separate experiments are involved with the spectrometer and each time the tuning characteristics differ. Also, if there are broad, overlapping lines, as was the case for mandelic acid, further uncertainty is added.

It appears that some of the most accurate data that can be gathered from an isofrequency plot are the g variation (Δg) between the maximum and minimum values of g for that plot, and the angle at which g_{max} occurs (θ_{max}). This gives six pieces of data from the three isofrequency plots. We need formulas relating these quantities to the principal values and eigenvectors of $\bar{\bar{g}}$.

At first we need to calculate the parameters β and γ as defined by consideration of the value of g at a specific magnetic orientation given by Equations (1) and (4) in Part II:

$$g^2 = \sum_{ij} W_{ij} \ell_i \ell_j = \alpha + \beta\cos 2\theta + \gamma\sin 2\theta \ ,$$

where $\overline{\overline{W}} = \overline{\overline{g}} \cdot \overline{\overline{g}}$ and the ℓ_i are direction cosines of the magnetic field vector with respect to the coordinate system. From Equation (29) of Part II, we have

$$\beta = \frac{1}{2} \sum_{ij} W_{ij} (S_i S_j - M_i M_j)$$

$$\gamma = \sum_{ij} W_{ij} S_i M_j \ , \qquad (36)$$

where S_i and M_i are the direction cosines of the vectors $\vec{S}$ and $\vec{M}$, which represent the magnetic field direction at the start of the isofrequency plot ($\theta = 0°$) and at the middle of the isofrequency plot ($\theta = 90°$).

There are two coordinate systems involved, one associated with the crystal axes, which is left unprimed, and one associated with the eigenvectors of the g tensor, which is primed. Using Figure 1b in Part II, we can write, in the crystal-axis coordinate system, for the three standard rotations about the orthogonal axes,

$$S_i = \delta_{is} \ , \ M_i = \delta_{im} \ , \ \ell_n = 0 \ , \ \ell_s = \cos\theta \ , \ \ell_m = \sin\theta \ , \qquad (37)$$

where the subscripts n,s,m refer to the rotation-, starting-, and middle-axis numbers. Putting Equation (37) into Equation (36) gives

$$\beta = \frac{1}{2}\,(W_{ss} - W_{mm})$$

$$\gamma = W_{sm} \cdot$$

In the principal-axis coordinate system of the g tensor we have

$$W'_{ii} = g_i^2 \,,$$

and to change into the unprimed system, we set

$$\overline{\overline{W}} = \overline{\overline{R}}^T \cdot \overline{\overline{W}}' \cdot \overline{\overline{R}}$$

$$W_{pq} = \sum_{ij} (R^T)_{pi} W_{ij} R_{jq} = \sum_{ij} R_{ip} g_i^2 \delta_{ij} R_{jq}$$

$$W_{pq} = \sum_i g_i^2 R_{ip} R_{iq}$$

$$\therefore \quad \beta = \frac{1}{2} \sum_i g_i^2 (R_{is}^2 - R_{im}^2)$$

$$\gamma = \sum_i g_i^2 R_{is} R_{im}$$

$$\theta_{ex} = \frac{1}{2} \arctan(\gamma/\beta) \,,$$

where θ_{ex} is an angle associated with g_{max} or g_{min} and the principal g-value eigenvectors in terms of the unprimed coordinate system are along the rows of $\overline{\overline{R}}$; or, likewise, the crystal-axis eigenvectors in terms of the primed coordinate system are along the columns of $\overline{\overline{R}}$. Since the arctangent function has two solutions 180° apart, we see that θ_{max} and

θ_{min} must be 90° apart. The two values for the extrema of g are calculated from Equation (22):

$$g_{ex}^2 = \sum_i g_i^2 \ell_i'^2(\theta_{ex})$$

$$\ell_i'(\theta_{ex}) = \sum_k (R^T)_{ik} \ell_k(\theta_{ex})$$

$$g = \{ \sum_{ik} g_i^2 R_{ki} \ell_i(\theta_{ex}) \}^{1/2},$$

where $\ell_n(\theta_{ex}) = 0$, $\ell_s(\theta_{ex}) = \cos\theta_{ex}$, $\ell_m(\theta_{ex}) = \sin\theta_{ex}$.

The g-value difference Δg is then $(g_{max}-g_{min})$.

It is impractical to determine the values of g_i and the eigenvector matrix $\bar{\bar{R}}$ from the values of Δg and θ_{max}. Instead, the formulas calculate Δg and θ_{max} for the three orthogonal rotations, given a specified g tensor. There are three independent parameters describing the eigenvector matrix, but there are nine elements in $\bar{\bar{R}}$. So instead of varying the elements in R, it is best to vary some set of three independent parameters and calculate R from them.

One such set is the Euler angles (α,β,γ) as defined by Rose.[94] We can construct an orthogonal matrix by using a formula by Rose.[95]

$$\bar{\bar{R}} = \begin{pmatrix} ca\cdot cb\cdot cc-sa\cdot sc & sa\cdot cb\cdot cc+ca\cdot sc & -sb\cdot cc \\ -ca\cdot cb\cdot sc-sa\cdot cc & -sa\cdot cb\cdot sc+ca\cdot cc & sb\cdot sc \\ ca\cdot sb & sa\cdot sb & cb \end{pmatrix} \tag{38}$$

$$ca \equiv \cos(\alpha)\ ,\ cb \equiv \cos(\beta)\ ,\ cc \equiv \cos(\gamma)$$

$$sa \equiv \sin(\alpha)\ ,\ sb \equiv \sin(\beta)\ ,\ sc \equiv \sin(\gamma)\ ,$$

A computer subroutine was written such that given three Euler angles, three principal g values, the experimental values for Δg and θ_{max}, and the corresponding weighting factors, it calculated the theoretical values for Δg and θ_{max} and determined a squared-difference-weighted error. This subroutine was used with a general minimization routine that varied the parameters to determine a minimum error. These subroutines are listed in Appendix I.

The $\bar{\bar{A}}$ tensor can likewise be calculated by using this procedure for the quantity gA, or A, as was discussed under Determination of ESR Parameters in the Theoretical Section.

RESULTS

I. X-ray Crystallography

The limiting conditions for reflection in terms of the hkl indices were determined as described in the Experimental section. These are listed in Table 1. There is a completely symmetric relationship among the hkl indices in these rules. By comparing these conditions with those listed in the International Tables,[96] it was determined that the space group is Pbca. This space group has four equivalent right-handed positions related by three screw axes about the a,b, and c axes. It also has four left-handed positions which are similarly related. These eight positions could be considered as corresponding with the four d-mandelic acid and the four l-mandelic acid molecules in the unit cell.

II. Irradiation and Spectra

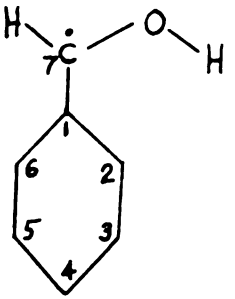
The crystals generally were irradiated with a ^{60}Co γ-ray source at a dose of 3×10^6 rads. This treatment caused the crystals to change from a colorless to a slightly yellow appearance. When single crystals of dl-mandelic acid were irradiated at 77°K, and the ESR spectrum was

Table 1.--Conditions limiting the possible reflections for dl-mandelic acid.

Indices	Conditions
h k l	: no conditions
0 k l	: k = 2n
h 0 l	: l = 2n
h k 0	: h = 2n
h 0 0	: (h = 2n)
0 k 0	: (k = 2n)
0 0 l	: (l = 2n)

Table 2.--Values of the hyperfine splitting constants of the alpha-hydroxybenzyl radical in various solutions and in a single crystal matrix.

Environment	$A(H_7)$	$A(H_2)$	$A(H_4)$	$A(H_6)$	$A(H_3)$	$A(H_5)$	$A(H_8)$	Reference
Benzyl alcohol soln	15.17	4.62	5.88	5.17	1.63	1.63	<0.47	97
Benzyl alcohol soln	14.97	4.58	5.93	5.16	1.56	1.67	0.58	98
Ethanol soln	14.93	4.56	5.92	5.14	1.56	1.67	0.64	99
Isopropyl alcohol soln	14.95	4.61	5.94	5.17	1.57	1.70	0.65	99
Tetrahydrofuran soln	14.93	4.64	5.95	5.17	1.54	1.65	0.60	99
Ethanol soln	14.89	4.59	5.92	5.15	1.55	1.66	1.18	99
Average ESR	16.21	(5.04 - 5.56)						This work
ENDOR			5.83					This work



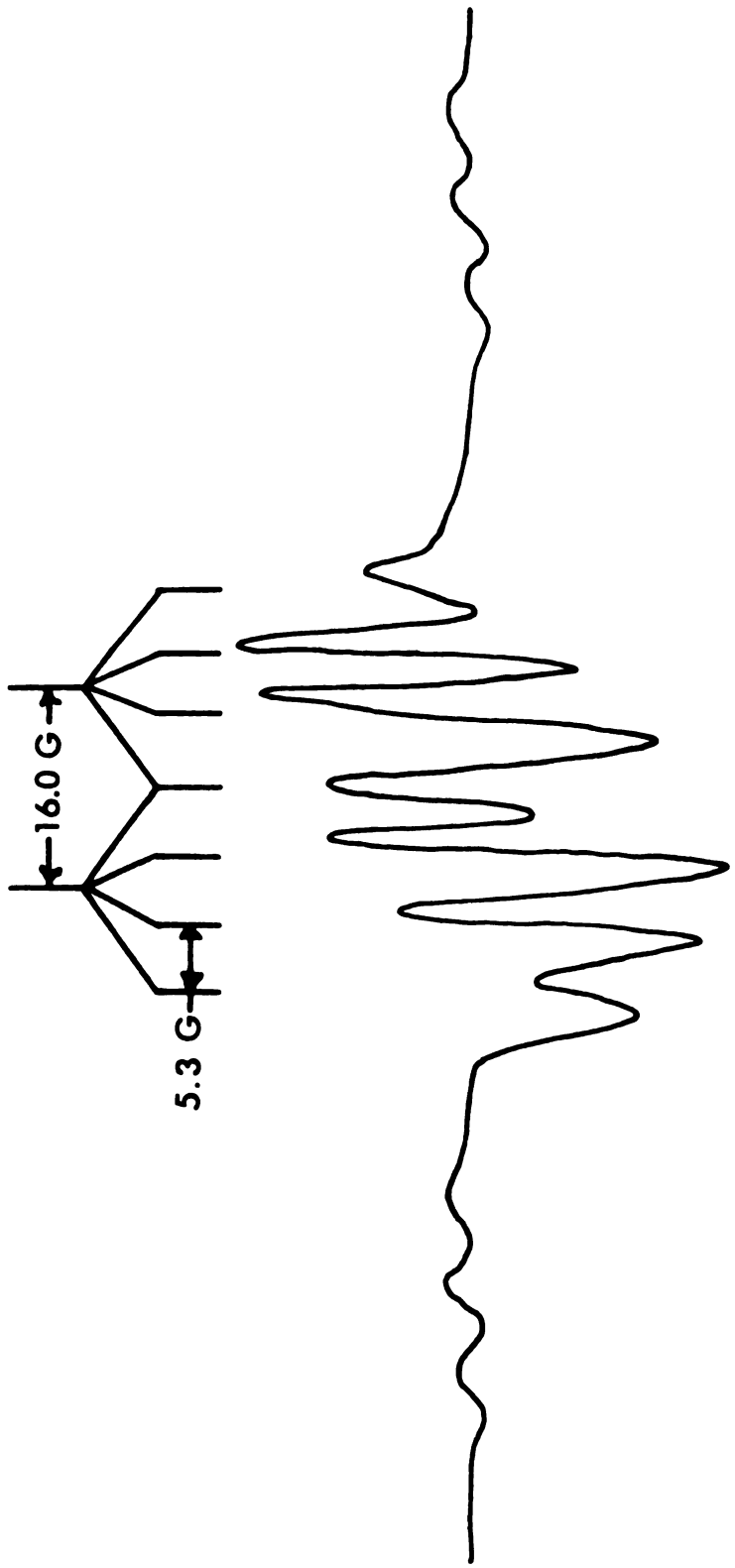


Figure 3. A typical ESR spectrum at room temperature of dl-mandelic acid irradiated at 77°K.

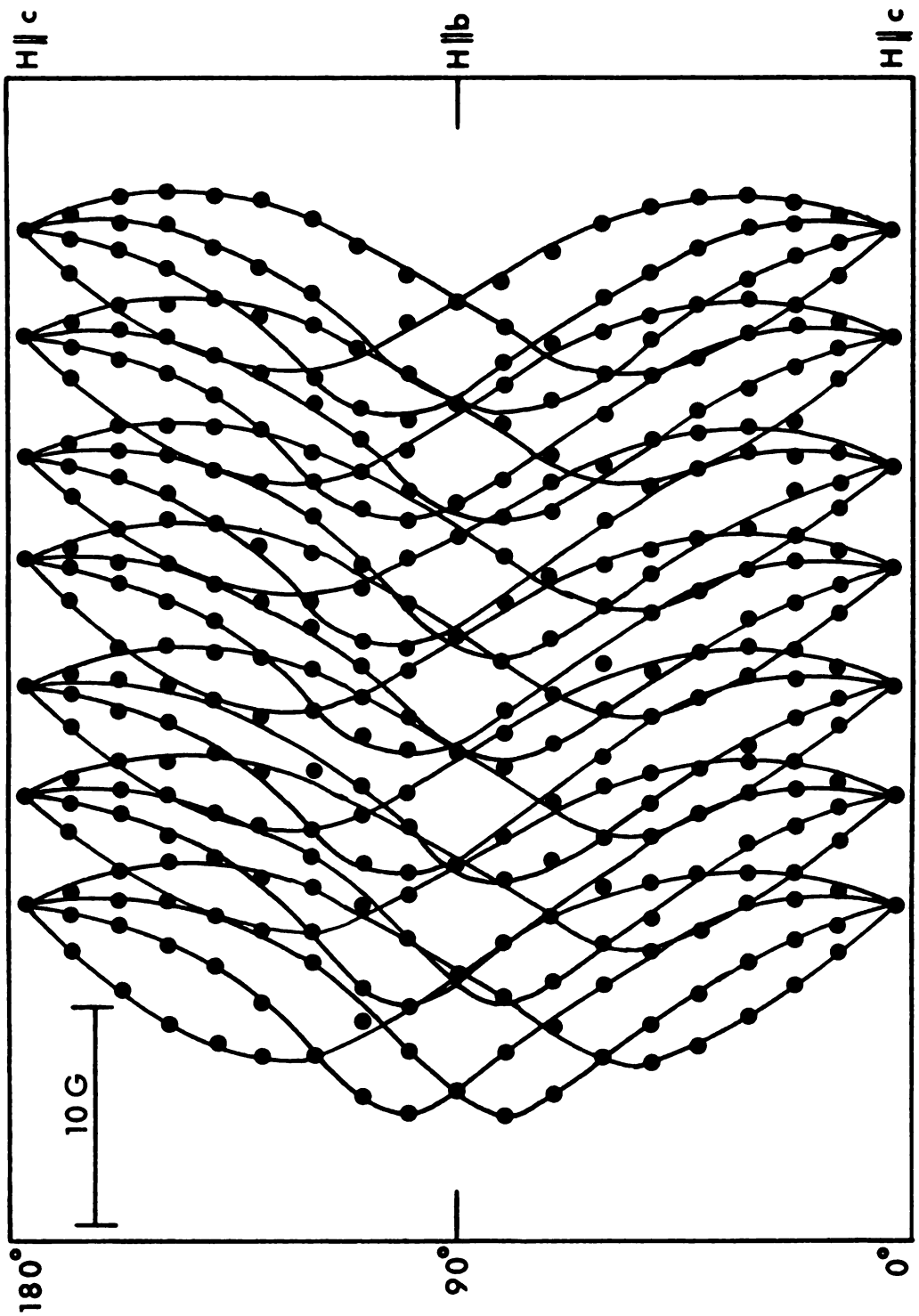


Figure 4. Plot of line positions for the alpha-hydroxybenzyl radical as a function of field orientation in the bc plane.

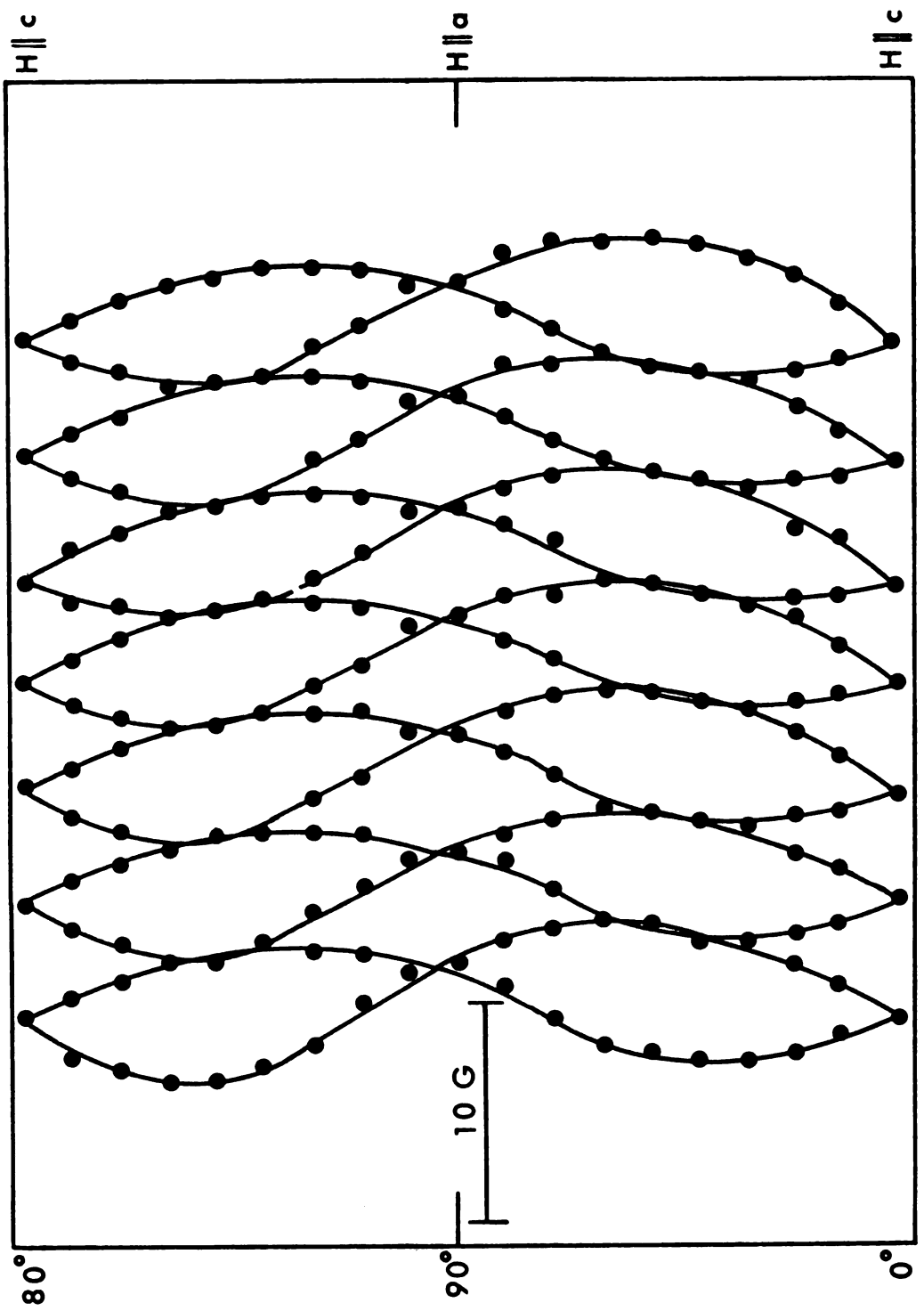


Figure 5. Plot of line positions for the alpha-hydroxybenzyl radical as a function of field orientation in the ca plane.

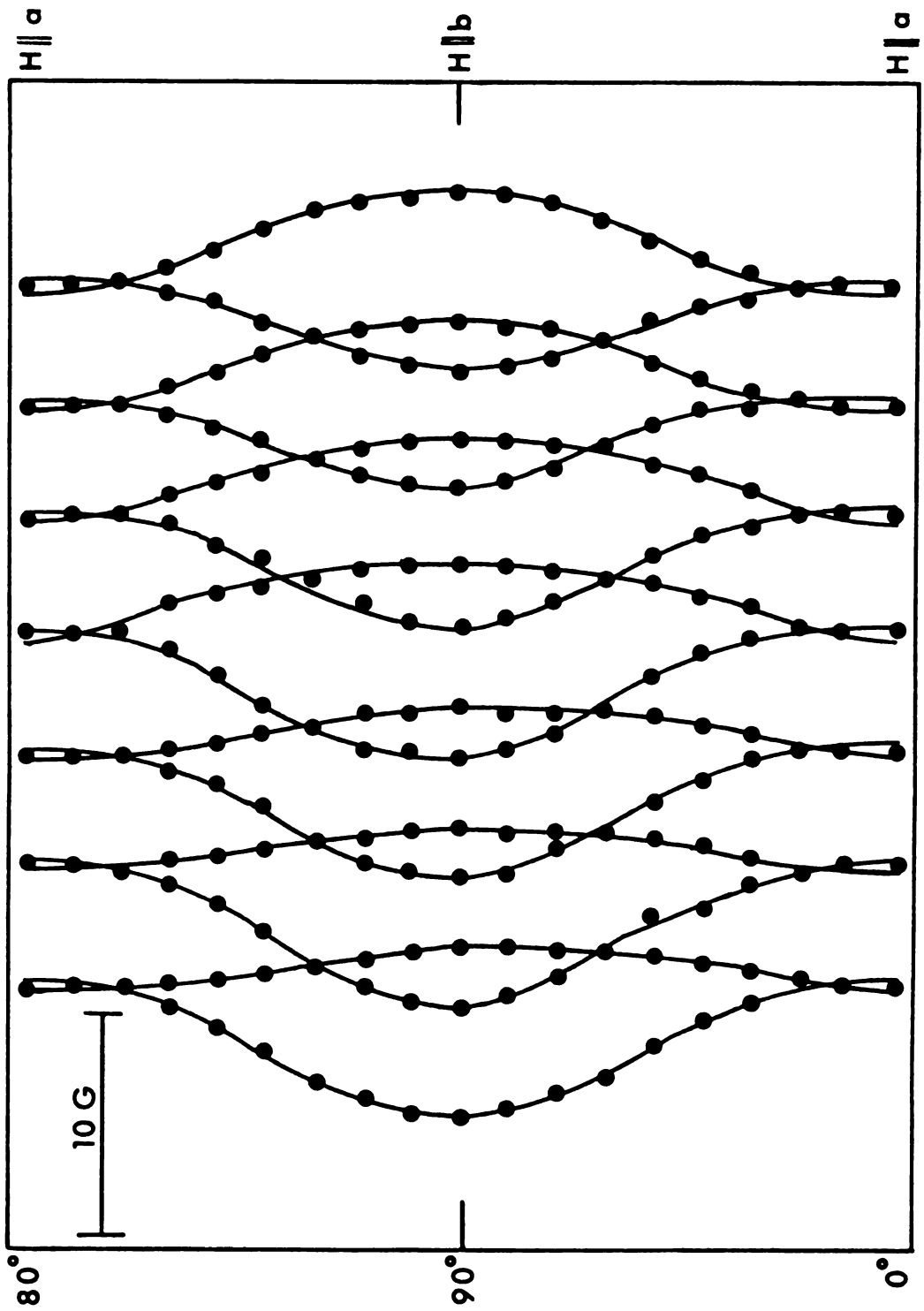


Figure 6. Plot of line positions for the alpha-hydroxybenzyl radical as a function of field orientation in the ab plane.

taken before the crystals were warmed up, it consisted of one very broad line at the free-spin value for electrons. Upon warming up, a "normal" spectrum resulted. When the crystals were recooled to 77°K, the same type of broad line resulted, but it was smaller in amplitude. A typical first-derivative normal spectrum is shown in Figure 3.

This spectrum consists of a central portion with large peaks, and two other portions on either side with considerably smaller peaks. The central portion consists of between seven and about twenty-two resonances over a range of about 33 gauss, centered approximately about the g free-spin value. The two groups of side peaks are symmetrically placed on either side of the central portion with a distance of about 92 gauss between the centers of the two groups. Each side portion consists of three to twelve resonances over a range of about 29 gauss.

III. Alpha-Hydroxybenzyl Radical

A. Determination of Radical

The central spectra can be analyzed as consisting of two sets of lines for the rotations about the b and c axes, and four sets of lines for the rotation about the a axis (Figures 4-6). Each set of lines consists of two groups of quartets which have one line overlapping to form seven lines (Figure 3). Since ^{12}C and ^{16}O have no magnetic moments, only the hydrogen nuclei produce hyperfine splittings. The observed set of lines could be produced

if one hydrogen caused a splitting of 16.0 gauss and three equivalent hydrogens produced a splitting of 5.3 gauss each.

We postulate that the species is the alpha-hydroxybenzyl radical, the alpha hydrogen causing the large splitting, the nearly equivalent ortho and para hydrogens the smaller splittings; the meta and hydroxyhydrogen splittings are too small to be observed in the broad lines. A comparison of the splittings for the alpha-hydroxybenzyl radical as reported in solution and the average ESR values of this investigation is shown in Table 2. The agreement appears good. Also, in the Table is listed the value of 5.83 gauss obtained from an ENDOR experiment on dl-mandelic acid consistent with the value for the para hydrogen.

B. g-Tensor Evaluation

We tried to use Schonland's method[93] of determining the tensor parameters for $\bar{\bar{g}}$ and $\bar{\bar{A}}$, but it failed. We then used the method described above in Parameters from Tensor Variations in the Experimental section. There was an ambiguity about which set of lines in each isofrequency plot belonged to a specific site of the radical. Each combination was tried in the six-parameter error-minimization routine also described above. We forced one of the principal values to remain the same during each computer run of this routine. We would then change this value independently to give the correct g-value average and give the other five final parameters as starting values

for another run of the program. This procedure stabilized the search for an absolute error minimum in the six-dimensional parameter space. At most four runs of the program were needed to reach a stable minimum. Although there was no guarantee that the minimum reached was not just a relative minimum, the searching method of the program was written to reduce this possibility.

One combination produced a considerably lower fitting-error than any other one. According to the space group of the undamaged crystal, there are four sites related by three twofold screw axes. To determine the eigenvectors of a radical related by a twofold screw about any axis, we need only change the signs of the direction cosines associated with that axis. When we formed these four theoretical isofrequency plots and put them together, they overlapped quite perfectly to form half of the sets of lines observed experimentally. Since the other half of the sets of lines were caused by the same radical, we tried to fit them by varying only the three Euler angles while keeping the same principal g values determined previously. Each remaining combination of lines was tried in a three-parameter minimization routine and one combination fit much better than the others. This second fit was not as good as the one obtained in the previous procedure. We now determined the remaining four sites required by the symmetry of the undamaged crystal. When all eight

theoretical plots were put together, they accounted for all the lines. The principal values, and direction cosines of the radical, for all eight sites are shown in Table 3 and the various site overlappings are shown in Table 4.

There are three causes for the large number of overlapping isofrequency curves. First, all the isofrequency plots have a near-mirror symmetry about the θ = 0° and θ = 90° positions (which point along crystal axes). This requires mathematically that sites must overlap in pairs. Secondly, the isofrequency plot for the ab plane shows that the extrema occur along the axes, which also requires sites to overlap in pairs. Thirdly, there is an accidental, experimental near-overlapping of lines for the rotation in the ac plane.

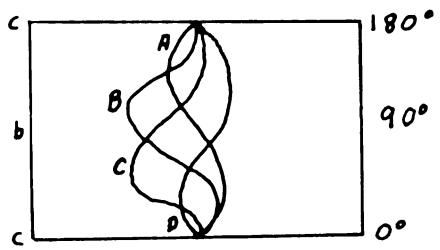
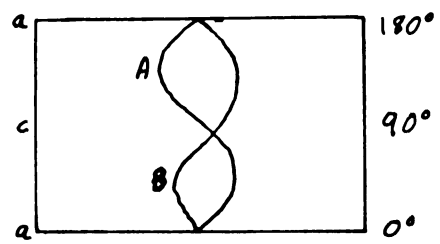
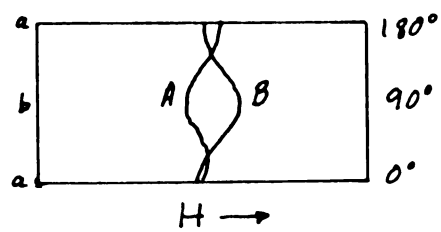
C. A-Tensor Evaluation.

The alpha hydrogen splitting was the only one whose anisotropy was large enough to be measured. Even in this case, there was a large scatter of experimental A-value points. This can be seen in Figures 7-10 where the A-value plots are labelled according to the g-value lines with which they are associated in Table 4. A rough calculation was made of the ratio between the fractional changes of the g and A tensors as defined in Equation (35). Since the ratio was small (0.008), we treated the A plots as representing a diagonalizable second-order tensor rather than the plots of the quantity gA.

Table 3.--The principal values and direction cosines for the g tensor and the alpha-hydrogen hyperfine splitting tensor of the alpha-hydroxybenzyl radical in dl-mandelic acid.

Principal Values	Direction Cosines			Signs for the Various Sites			
				site 1	site 2	site 3	site 4
	a	b	c	a b c	a b c	a b c	a b c
g_{11} = 2.0039	0.1867	0.9238	0.3342	- + +	+ - +	+ + -	- - -
g_{22} = 2.0022	0.4224	0.2317	0.8763	- + -	+ - -	+ + +	- - +
g_{33} = 2.0033	0.8870	0.3048	0.3469	+ + -	- - -	- + +	+ - +
				site 5	site 6	site 7	site 8
				a b c	a b c	a b c	a b c
g_{11} = 2.0039	0.9016	0.1608	0.4015	- + +	+ - +	+ + -	- - -
g_{22} = 2.0022	0.2169	0.6349	0.7415	- + -	+ - -	+ + +	- - +
g_{33} = 2.0033	0.3742	0.7557	0.5376	+ + +	- - +	- + -	+ - -
				site 1	site 2	site 3	site 4
				a b c	a b c	a b c	a b c
A_{11} = -18.33	0.0006	0.8137	0.5813	+ - -	- + -	- - +	+ + +
A_{22} = -15.33	0.4587	0.5164	0.7232	+ - +	- + +	- - -	+ + -
A_{33} = -14.97	0.8886	0.2670	0.3729	- - +	+ + +	+ - -	- + -
				site 5	site 6	site 7	site 8
				a b c	a b c	a b c	a b c
A_{11} = -18.33	0.5571	0.2181	0.8013	- + -	+ - -	+ + +	- - +
A_{22} = -15.33	0.6708	0.4506	0.5890	- + +	+ - +	+ + -	- - -
A_{33} = -14.97	0.4896	0.8657	0.1047	+ + -	- - -	- + +	+ - +

Table 4.--Correlation between the individual sites and the resulting overlapped lines for the alpha-hydroxybenzyl radical.

Axis of Rotation	Correlation of Sites to Lines	Center-of-Spectrum Lines
a	Site: 1 2 3 4 5 6 7 8 Line: B C C B A D D A	
b	Site: 1 2 3 4 5 6 7 8 Line: B A B A B A B A	
c	Site: 1 2 3 4 5 6 7 8 Line: A A A A B B B B	

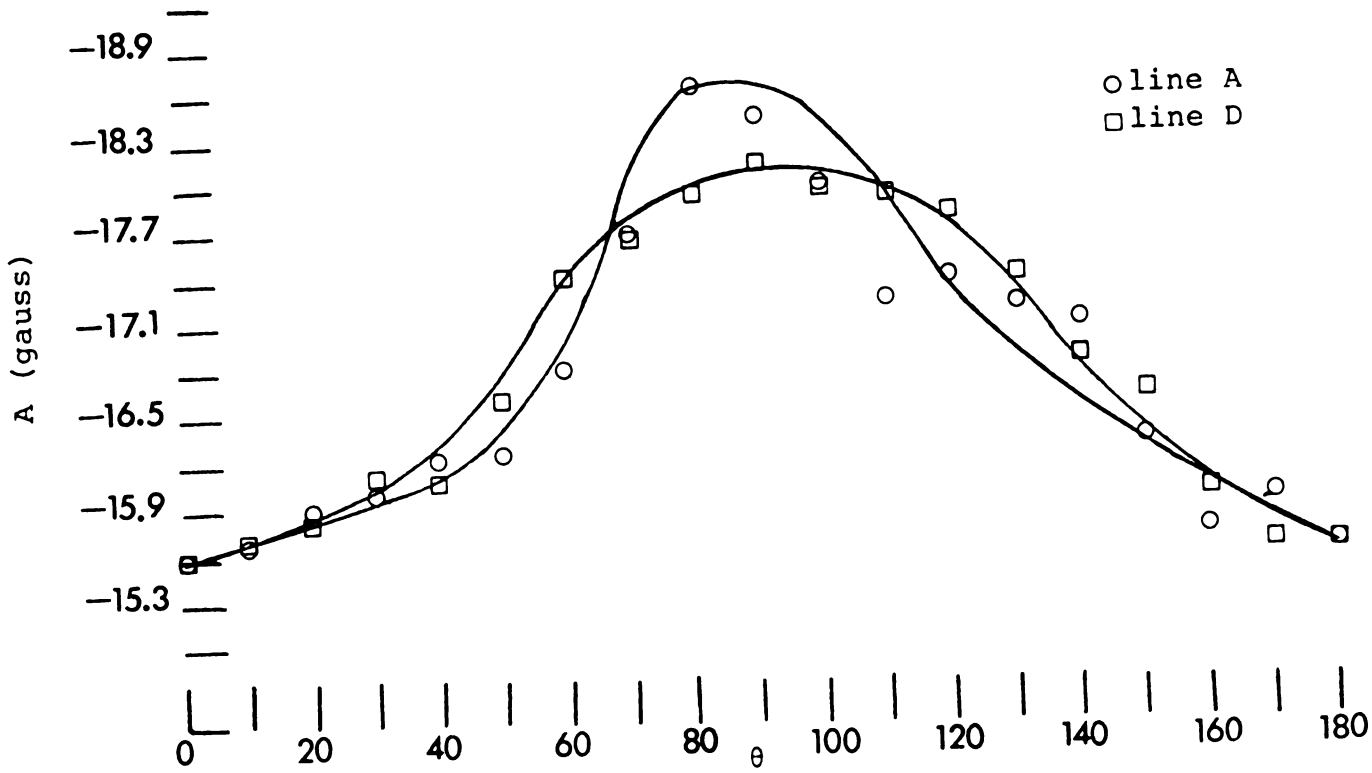


Figure 7. Hyperfine splitting of the alpha proton of the alpha-hydroxybenzyl radical vs. angle of rotation in the bc plane for lines A and D.

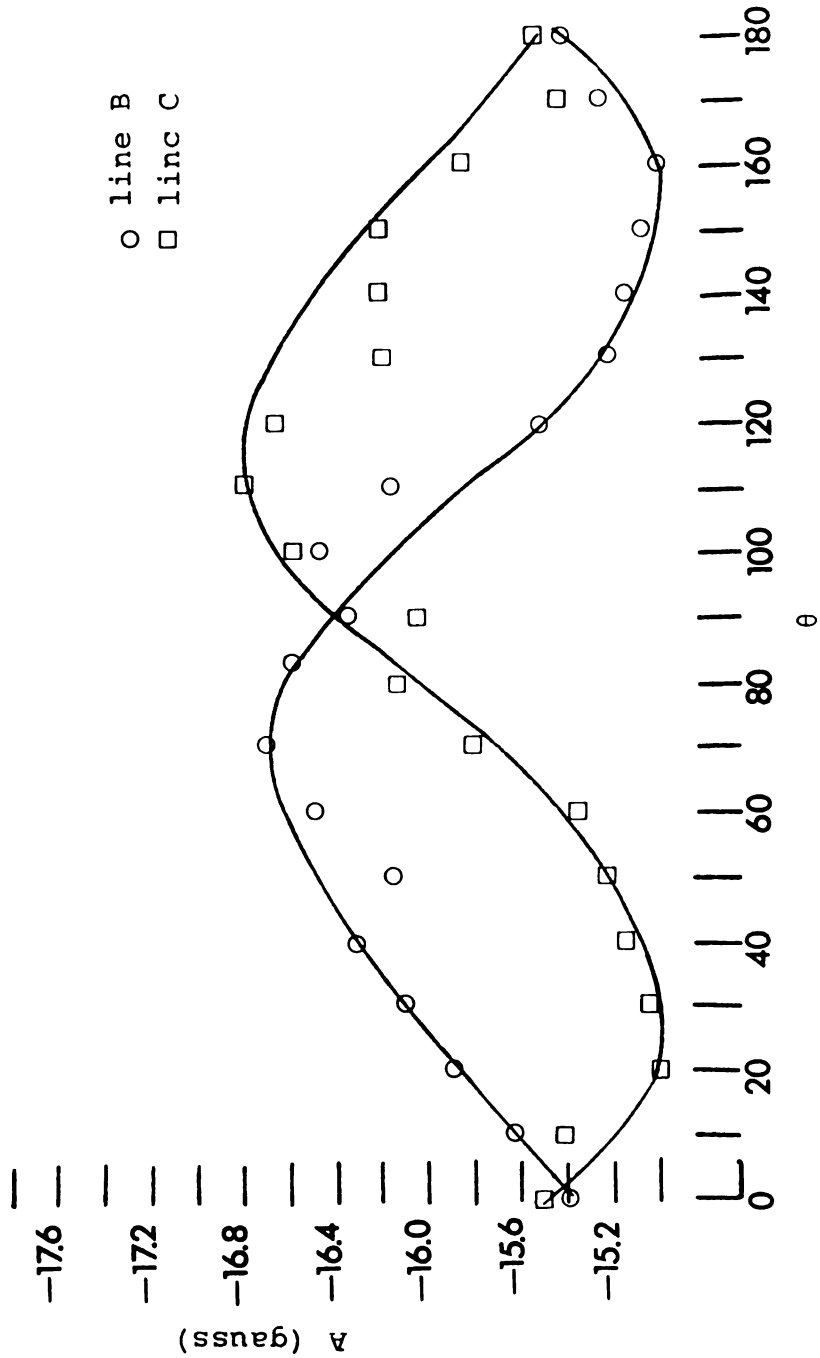


Figure 8. Hyperfine splitting of the alpha proton of the alpha-hydroxybenzyl radical vs. angle of rotation in the bc plane for lines B and C.

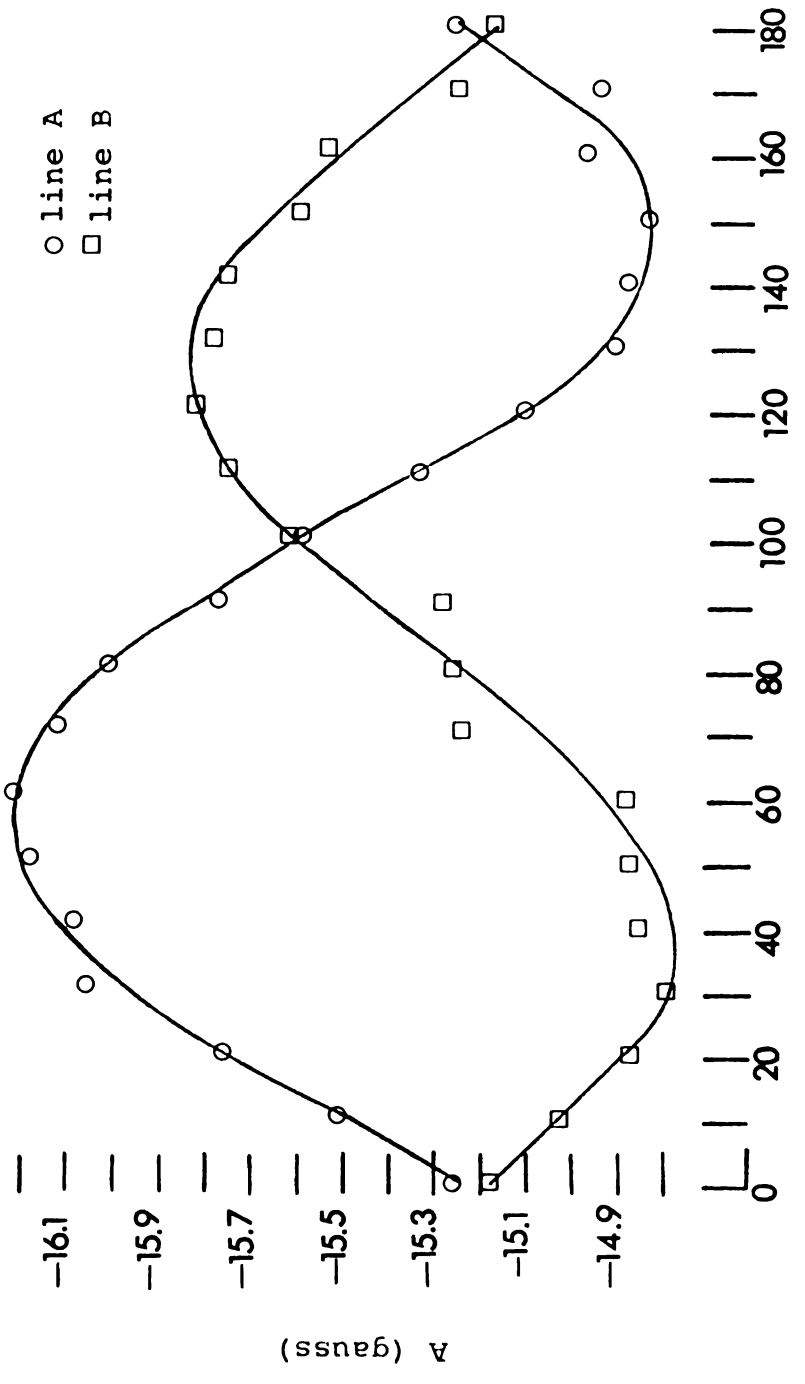


Figure 9. Hyperfine splitting of the alpha proton of the alpha-hydroxybenzyl radical vs. angle of rotation in the ca plane.

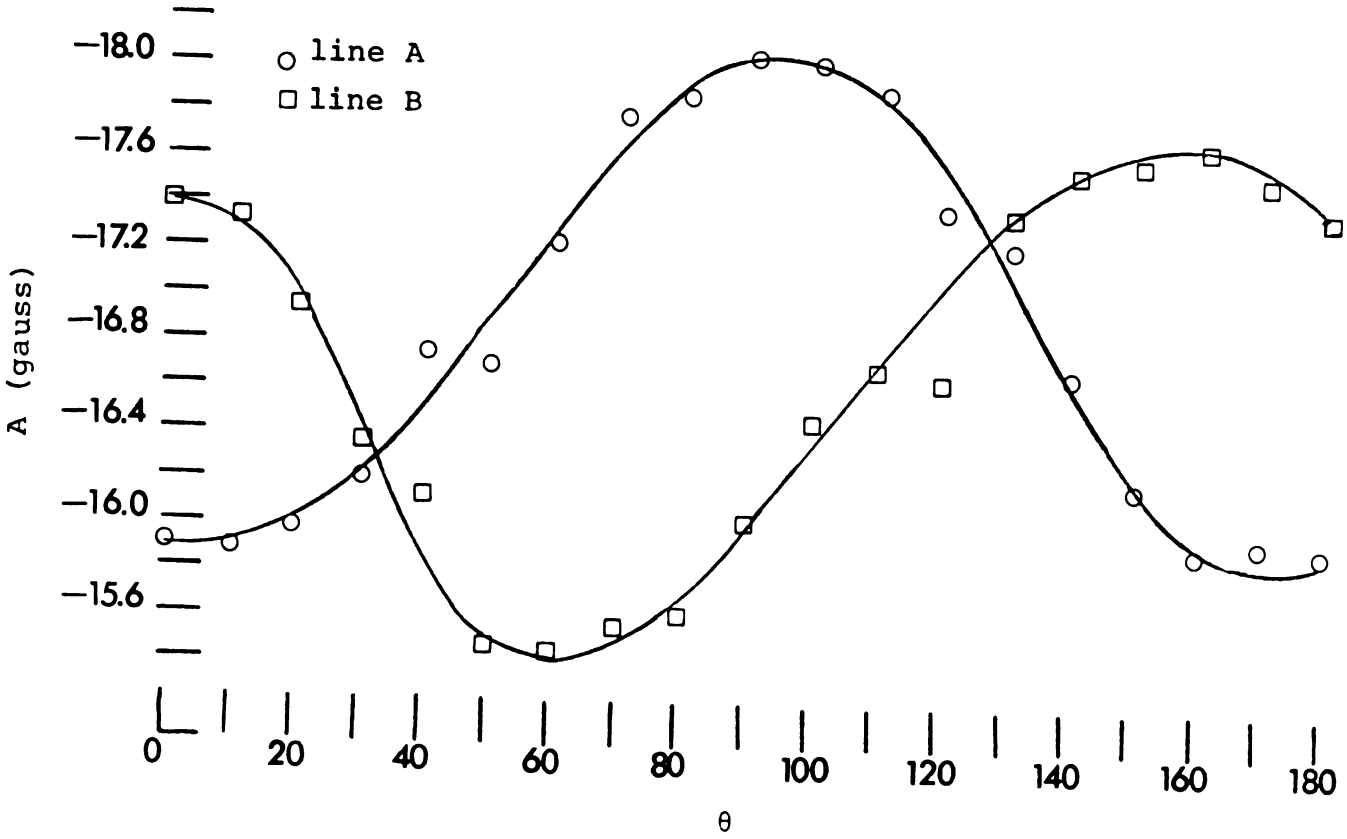


Figure 10. Hyperfine splitting of the alpha proton of the alpha-hydroxybenzyl radical vs. angle of rotation in the ab plane.

Using the experimental values for ΔA and θ_{max} for the A-value plots, we again used the six-parameter minimization routine on each combination of lines. One combination of lines had a considerably smaller fitting-error than the other ones. This set of A-value lines corresponded to the same g-value lines (site 1) which had given the best fit for the g tensor. Again using Equation (38), we produced a matrix $\bar{\bar{A}}_v$ representing the eigenvectors of A for site 1.

Since the A and g tensors are for the same radical, it was expected that the tensors were similarly related to each other for all eight sites. Because of the similar symmetry of the A and g plots, we could also produce half of the A-value line sets by applying the same three screw-axis-transformations to $\bar{\bar{A}}_v$. This trivially guaranteed that the g and A tensors were similarly related for sites 1,2,3, and 4. For the g tensor, sites 5,6,7, and 8 were symmetrically related to each other, and site 5 was related to site 1 by some nonsymmetric similarity transformation matrix which was calculated. By applying this transformation to $\bar{\bar{A}}_v$, we produced A-tensor eigenvectors for site 5 that had the proper relationship to the g tensor for site 5. We again derived the A-tensor eigenvectors for sites 6,7, and 8 from the one for site 5 by applying the screw-axis operations. When all eight A tensors were considered together, they accounted for all of the lines in the A

plots. The principal A values and direction cosines of the alpha-hydrogen splitting for all eight sites are shown in Table 3.

D. Variable Temperature Study

A variable temperature ESR study of the alpha-hydroxybenzyl radical was done. The Q-band instrument was used and the temperature was varied from -150°C to +120°C. There was no discernible difference in the spectra.

IV. Cyclohexadienyl-Glycolic Acid Radical

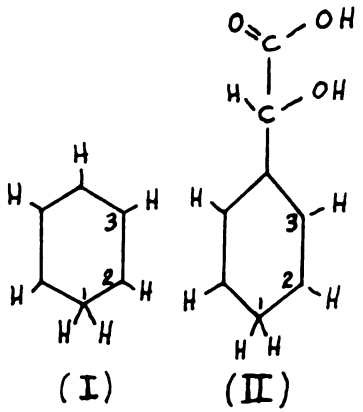
A. Determination of Radical

From the spectrum shown in Figure 11, we see that each set of peaks can be analyzed as consisting of a triplet of triplets with splittings of 8.99 gauss and 2.65 gauss. The large 95.5 gauss separation would not normally be caused by a hydrogen atom, so we can assume that there is a triplet splitting of 47.7 gauss. The middle portion of the spectrum would be lost in the larger peaks of the alpha-hydroxybenzyl radical.

We postulate that the side peaks are caused by the cyclohexadienyl-glycolic acid radical. A comparison of the splittings for this radical as reported in solution with the average ESR values of this work is shown in Table 5. The agreement appears good. We attribute the largest triplet splitting to the two para protons, the second

Table 5.--Values of the hyperfine constants of the cyclohexadienyl-glycolic acid radical in various solutions and in a single-crystal matrix.

Environment	A_1	A_2	A_3	Reference
(I) in benzene soln	47.5	10.4	2.5	100
(I) in 1,4-cyclohexadiene soln	47.71	8.99	2.65	101,102
Average ESR of (II) (Single-Crystal)	46.4	8.56	3.0	This work



(I) (II)

Table 6.--Correlation between the individual sites and the resulting overlapped lines for the cyclohexadienyl-glycolic acid radical.

Axis of Rotation	Correlation of Sites to Lines	A-value Plots
a	Site: 1 2 3 4 Line: Z Y Y Z	
b	Site: 1 2 3 4 Line: Y Z Y Z	
c	Site: 1 2 3 4 Line: Z Z Y Y	

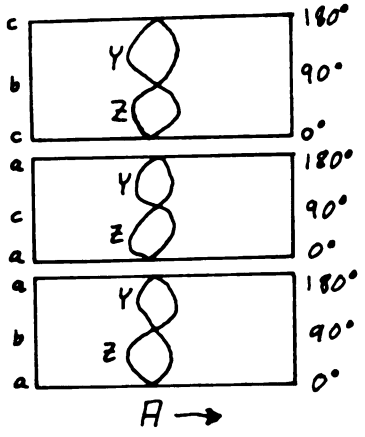
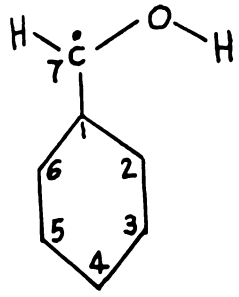


Table 7.--The principal values and direction cosines for the CH_2 hyperfine splitting tensor of the cyclohexadienyl-glycolic acid radical in dl-mandelic acid.

Principal Values	Direction Cosines			Signs for the Various Sites			
				site 1	site 2	site 3	site 4
	a	b	c	a b c	a b c	a b c	a b c
A_{11} = -28.50	0.6323	0.5228	0.5717	- + -	- + +	- - -	+ + -
A_{22} = -52.48	0.7236	0.1350	0.6769	+ + -	+ + +	+ - -	- + -
A_{33} = -57.26	0.2767	0.8417	0.4637	- - -	- - +	- + -	+ - -

Table 8.--Unpaired electron spin and excess charge densities calculated for the alpha-hydroxybenzyl radical by the McLachlan method.[107]

Atom	ρ	ε
C_1	0.001	-0.053
C_2	0.159	-0.036
C_3	-0.053	0.034
C_4	0.214	-0.145
C_5	-0.065	0.054
C_6	0.187	-0.108
C_7	0.489	0.028
O	0.067	-0.774



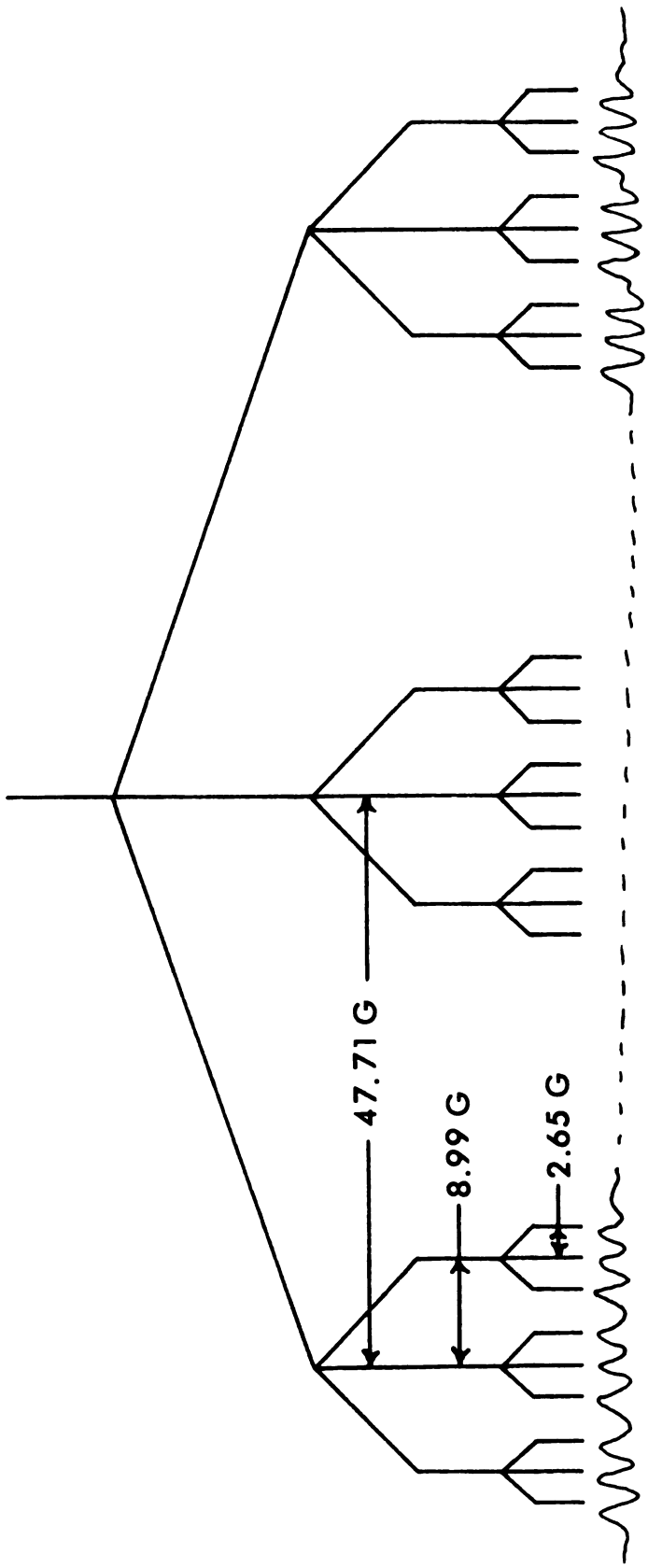


Figure 11. The wing lines of an ESR spectrum at room temperature of dl-mandelic acid irradiated at 77°K.

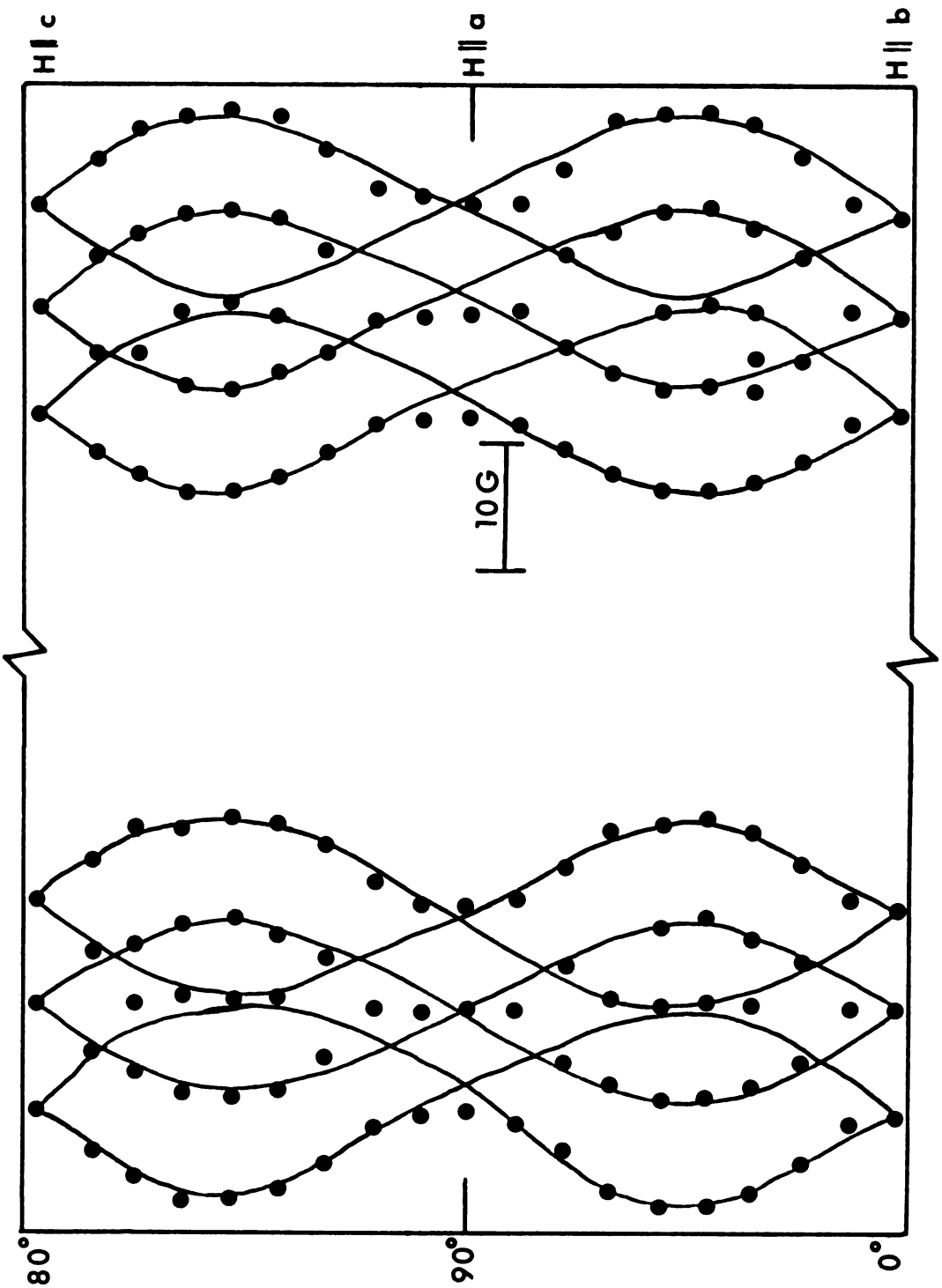


Figure 12. Plot of line positions for the cyclohexadienyl-glycolic acid radical as a function of field orientation in the ca plane.

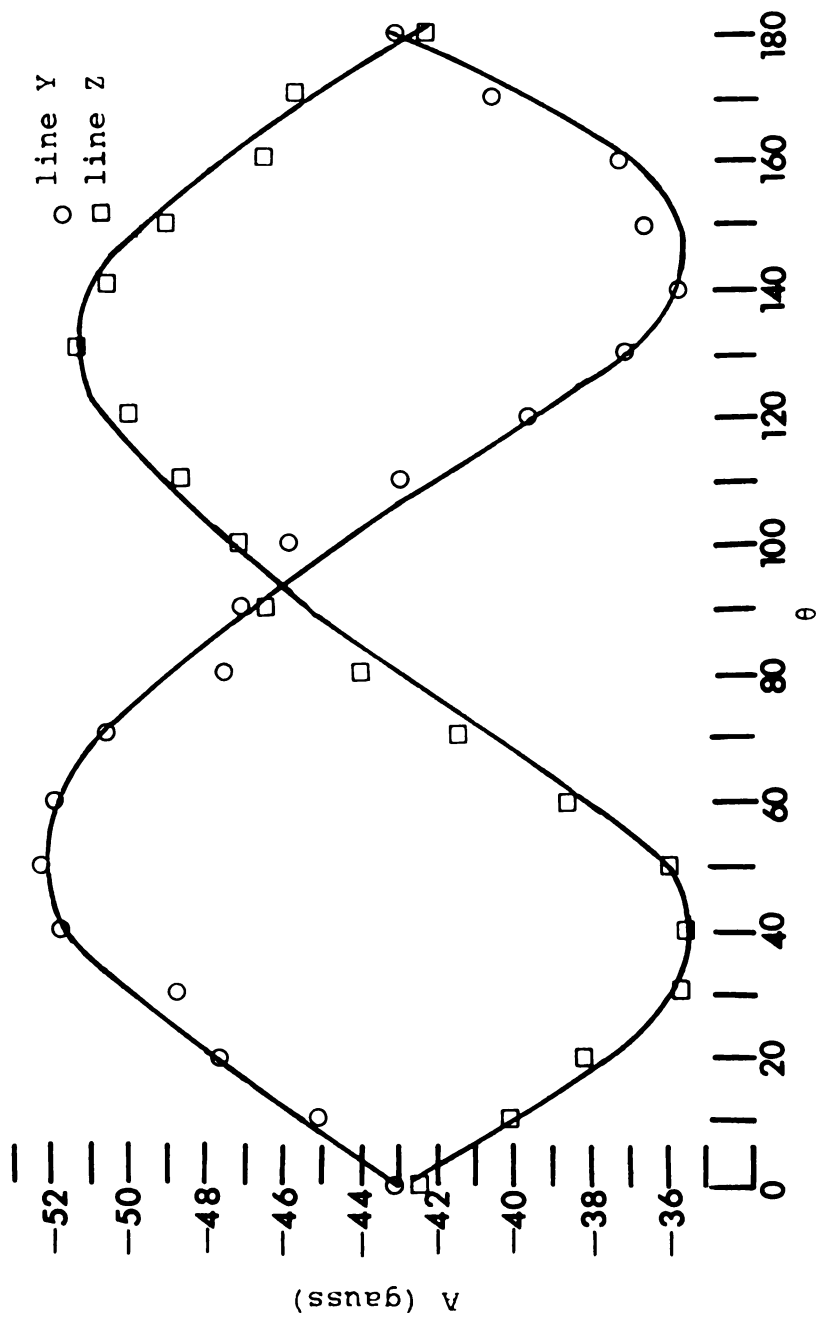


Figure 13. The CH_2 hyperfine splittings of the cyclohexadienyl-glycolic acid radical vs. angle of rotation in the bc plane.

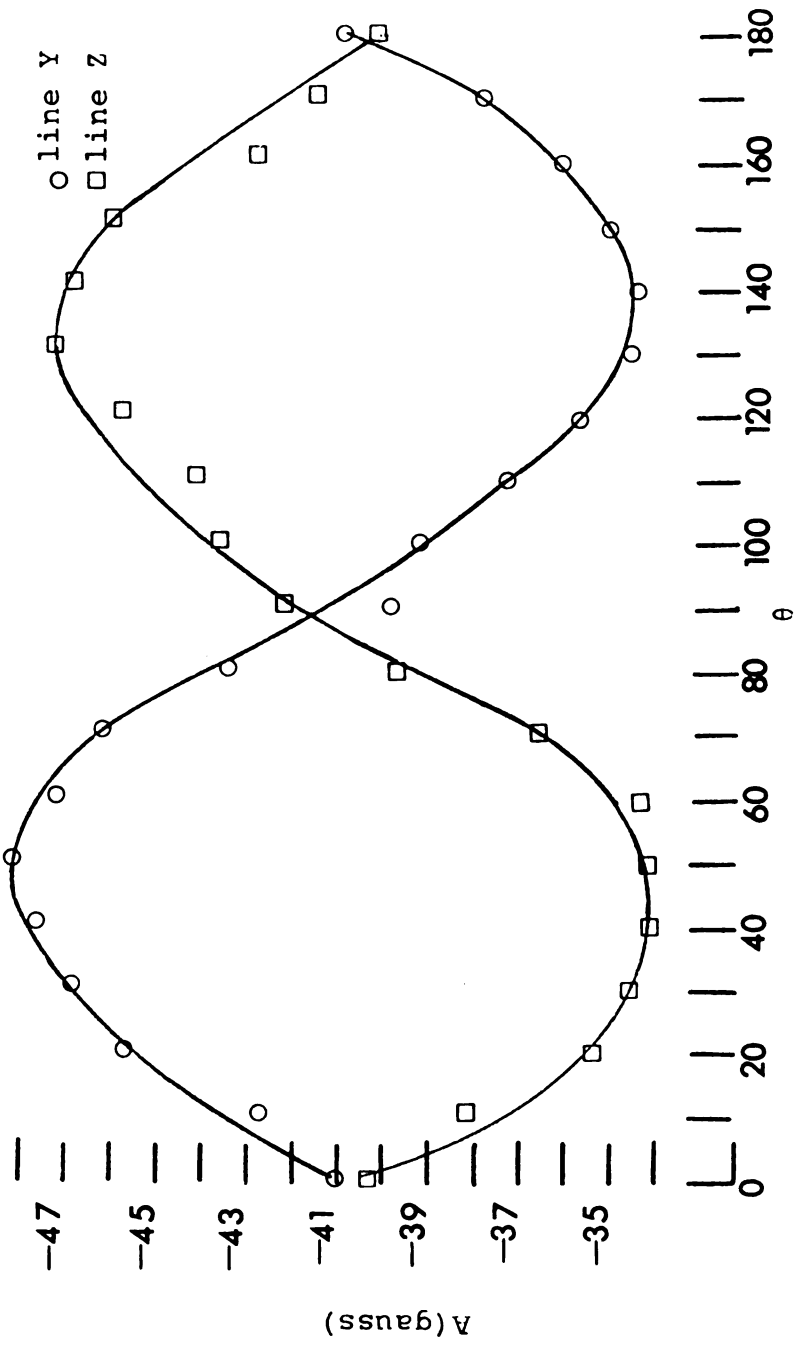


Figure 14. The CH_2 hyperfine splittings of the cyclohexadienyl-glycolic acid radical vs. angle of rotation in the ca plane.

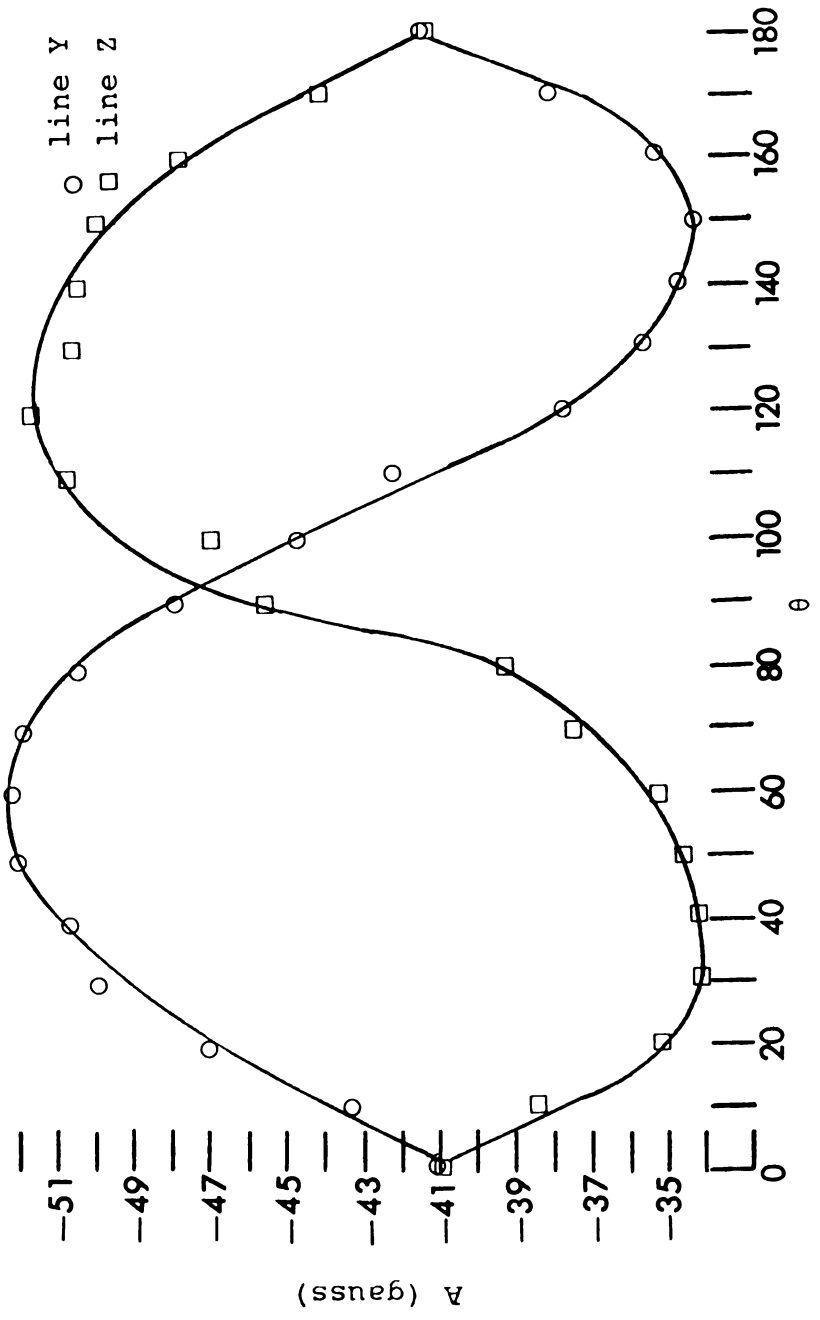


Figure 15. The CH_2 hyperfine splittings of the cyclohexadienyl-glycolic acid radical vs. angle of rotation in the ab plane.

largest triplet splitting to the two meta protons, and the smallest triplet splitting to the two ortho protons.

This second radical is found under more stringent conditions than the main radical. Irradiation of dl-mandelic acid at room temperature gives the main radical but not the second radical. Irradiation of d-mandelic or l-mandelic acid at either 77°K or room temperature appear to give the main radical. The lines of the side radical, if formed, are considerably weaker than in the case of its formation when dl-mandelic acid is irradiated at 77°K.

B. g-Value and A-Tensor Evaluation

In the ab plane, the isofrequency plot for the side radical showed a clear pattern of twelve lines paired into two sets of six lines. This is shown in Figure 12. The ortho proton splitting was discernable only on some outer lines for some orientations. The other planes had similar isofrequency plots, but only the outer line positions could be clearly followed throughout the rotation. The A-value plots for the CH_2 splitting are shown in Figures 13-15 where the plots are labelled according to the scheme in Table 6.

The data from the isofrequency plots were not precise enough to determine any g-tensor anisotropy. The isotropic value for g was calculated to be 2.0026.

The anisotropy of the CH_2 splitting was considerable. We used the same procedure as described for the alpha-hydroxybenzyl radical to determine the tensor

parameters. There were two A-plot curves for each rotation. This gave eight combinations of lines. One combination gave a drastically lower fitting-error than the others. The eigenvectors of this site were transformed into the eigenvectors of the other three sites by performing the three twofold screw axis operations on them. When these theoretical plots were considered together, they accounted for all of the A-value curves. The principal values and direction cosines of the radical for all four sites are shown in Table 7 and the various site overlappings are shown in Table 6.

C. Variable-Temperature Study

A variable temperature ESR study of the cyclohexadienyl-glycolic acid radical was made. The Q-band instrument was used and the temperature was varied from -150°C to +120°C. As in the case of the alpha-hydroxybenzyl radical, no significant differences were observed in the spectra with change in temperature.

V. Electron Irradiation at 77°K

A single crystal of dl-mandelic acid was irradiated at 77°K with a dose of 6×10^7 rads using the 1 Mev electron source described in the Experimental section. This treatment caused the crystal to turn slightly yellow as was the case on γ-irradiation. The spectra were identical to the ones obtained from γ-irradiation at 77°K.

VI. d-Mandelic Acid and l-Mandelic Acid Irradiation

d-Mandelic acid and l-mandelic acid in powdered form were obtained from Aldrich Co. All crystals were grown from saturated aqueous solutions by slow evaporation. The crystal system of d-mandelic acid was reported to be monoclinic[103] while that of l-mandelic acid was orthorhombic.[104] The morphology of the d-mandelic acid crystals agreed with that reported in the literature and this was similarly true for the l-mandelic acid crystals.

d-Mandelic acid crystals were γ-irradiated at room temperature and their spectra were taken on the Q-band spectrometer at various orientations. These spectra had the same type of seven-line pattern with no side peaks as was found for the case of dl-mandelic acid irradiated at room temperature. When d-mandelic acid was irradiated at 77°K, it still showed the same spectra with no side peaks while the spectra of dl-mandelic acid irradiated at 77°K would have the extra side peaks. This showed that the alpha-hydroxybenzyl radical is formed in both the d- and dl-mandelic acid crystals at either 77°K or room temperature, but that the cyclohexadienyl-glycolic acid radical is formed only in dl-mandelic acid at 77°K an never in d-mandelic acid.

The same procedure was applied to l-mandelic acid with the same results. Only the alpha-hydroxybenzyl

radical is formed when l-mandelic acid is irradiated at 77°K or room temperature.

DISCUSSION

I. Alpha-Hydroxybenzyl Radical

The alpha-hydroxybenzyl radical appears to be formed by the removal of a carboxyl group from a d- or l-mandelic acid molecule. It is assumed that the hydrogen and hydroxy groups would move from their original tetrahedral configuration about the central carbon atom to give a planar species.

To check the geometry of this radical, energy calculations were made for various configurations using INDO.[105] At first, we varied the positions of the CHOH atoms in the plane of the benzene ring using previously determined parameters for the benzyl radical[106] until an energy minimum was reached. It was then found that any rotation of the CHOH group produced a higher energy. Therefore, INDO calculations would predict a planar radical. The final parameters which minimized the energy are shown in Figure 16.

As was discussed in the section on Results, the central isofrequency lines were accounted for by assuming that there were two sets of four sites. In each group, the four sites were related by the three twofold

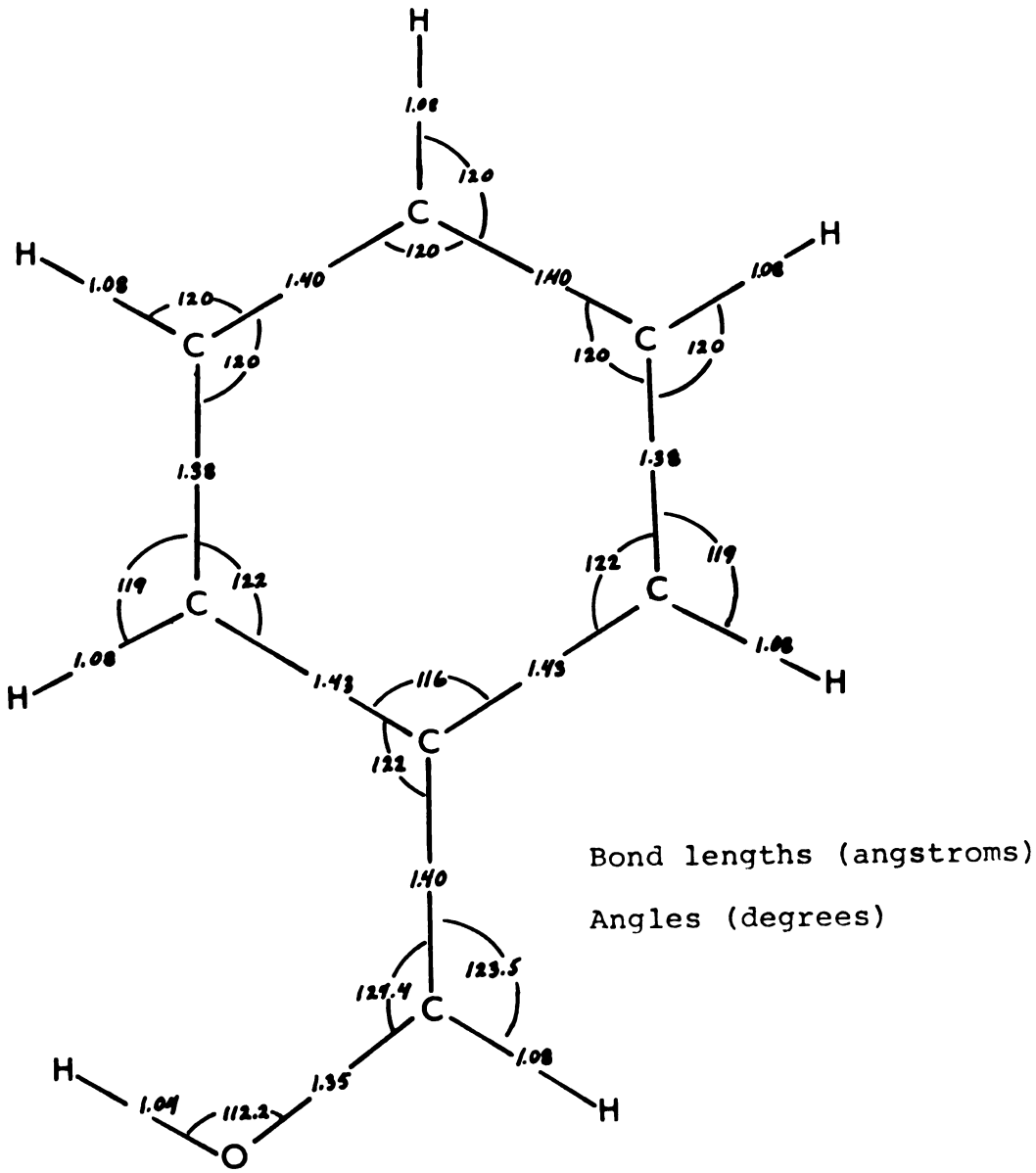


Figure 16. The atom positions of the planar alpha-hydroxybenzyl radical as calculated by INDO.

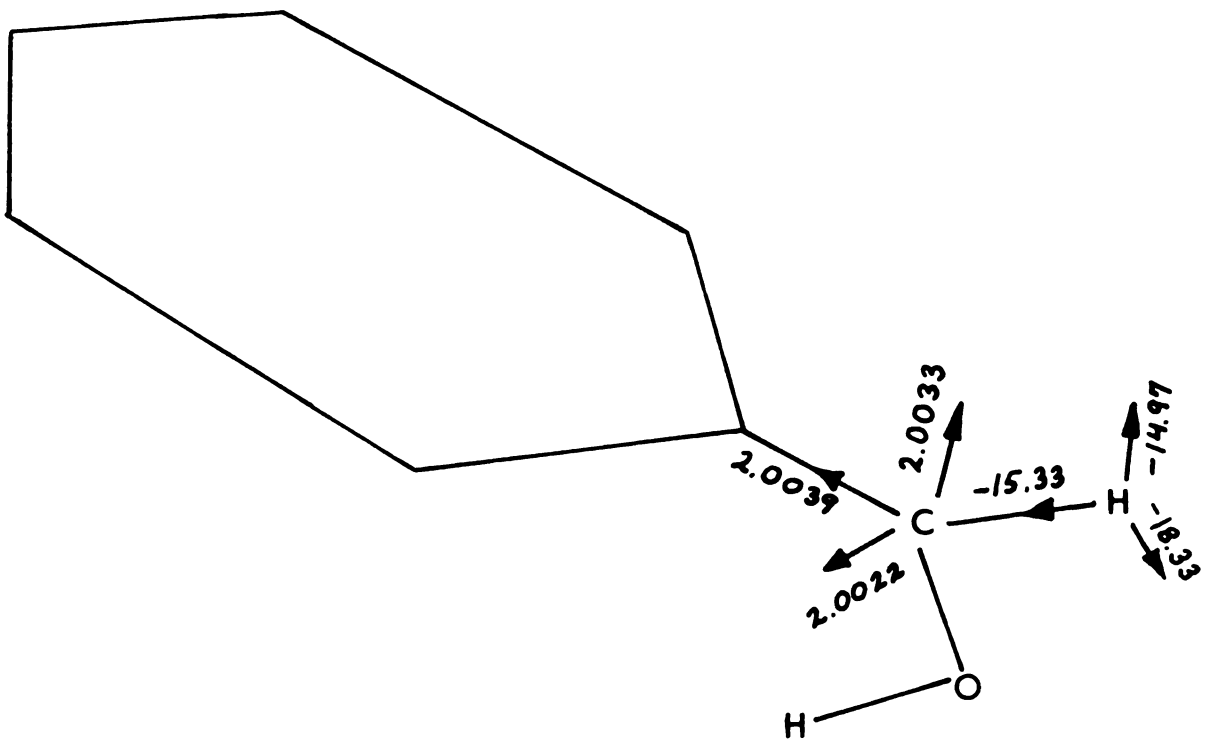


Figure 17. The relationship between the eigenvectors of the g and A tensors and the geometry of the planar alpha-hydroxybenzyl radical. The g = 2.0033 and $A(H_\alpha)$ = -14.97 directions are perpendicular to the plane of the radical and the remaining eigenvectors are in the plane (the geometry of the radical is assumed to be as in Figure 16).

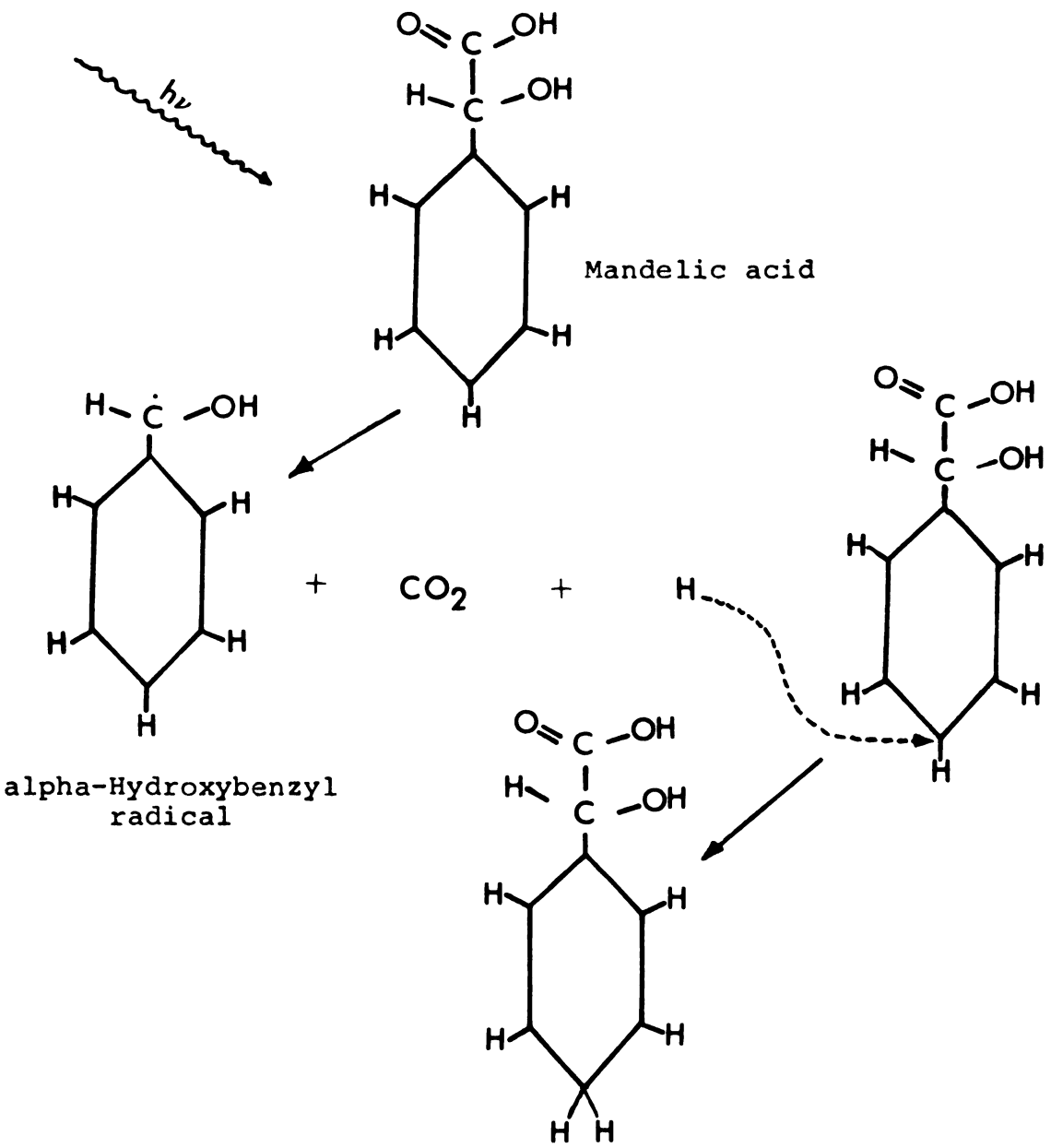


Figure 18. A possible scheme for the formation of the two radicals in the irradiation of dl-mandelic acid at 77°K.

screw axes. The undamaged crystal had two sets of four molecules per unit cell, one set being d-mandelic acid molecules and the other being l-mandelic acid molecules. We could deduce then that sites 1,2,3, and 4 of Table 3 correspond to the d-mandelic acid species and sites 5,6,7, and 8 correspond to the l-mandelic acid species, or vice versa.

In the undamaged crystal, the d- and l-mandelic acid molecules are related by a center of inversion. This would require that the benzene ring plane of each of the four sites of the d-mandelic acid molecules must be parallel to the benzene ring plane of a corresponding l-mandelic acid molecule. Because the alpha-hydroxybenzyl species ia a pi-electron radical, we would expect that one of the principal axes of the g tensor would be perpendicular to the radical plane and thus to the benzene ring plane. Then, if the benzene ring planes did not reorient when the crystal was damaged, we would expect that one eigenvector in each of the sites 1,2,3, and 4 would be parallel to the eigenvectors in each of the sites 5,6,7, and 8. It is evident from Table 3, that this is not the case. We would conclude that the benzene ring planes change their orientation significantly as a result of the radiation.

Previous calculations of the spin densities for the alpha-hydroxybenzyl radical have been made[107] by using McLachlan's approximate self-consistent field method.[108]

An "excess charge density" was also calculated by using the relation proposed by Colpa and Bolton,[109, 110]

$$a = (Q + K\varepsilon)\rho,$$

where a is the isotropic proton hyperfine coupling constant, ε the excess charge density, ρ the unpaired electron spin density on the adjacent carbon atom, and Q and K are constants that were chosen to be -30 gauss and -15 gauss, respectively, to give the best fit to the values of a. This relationship was used instead of McConnell's equation because it produces better results for radicals in which there is an appreciable excess charge, or considerably different excess charges at various sites of the radical, both conditions of which apply to the alpha-hydroxybenzyl radical. The results are listed in Table 8.

It was found that the relationship between the eigenvectors of the g and A tensors could be related to the geometry of the molecule. This is shown in Figure 17, where the principal g and A values correspond to those in Table 3. In this figure, the eigenvectors of the g tensor point so that g_{33} is perpendicular to the CHOH plane, $g_{11}=g_{max}$ points along the exocyclic carbon-carbon bond, and $g_{22}=g_{min}$ is orthogonal to g_{11} and g_{33}. Assuming this, it was then found that the eigenvectors of the A tensor of the alpha hydrogen point so that $A_{33}=A_{min}$ is perpendicular to the CHOH plane within 2°, A_{22} points along the C-H bond within 15°, and $A_{11}=A_{max}$ is orthogonal to A_{11} and A_{33}.

If we subtract the isotropic value of -16.21 gauss from the principal values of $A(H_7)$ in Table 3, we obtain (-2.12,+0.88,+1.24) gauss for the anisotropy of the alpha-proton. The typical values for alpha-proton anisotropy are (-10.0,+10) gauss.[26] One theoretical approach[111] to calculating the anisotropy approximates it as a magnetic dipole interaction between the hydrogen and the electron spin magnetization that is distributed in the 2s and 2p atomic orbitals on the neighboring carbon atom. This treatment gives values of (-14,-2,+15) gauss for a case of one pi electron on the adjacent carbon atom. If we consider the dipole effect to be proportional to the unpaired spin density on the carbon atom and use the value of 0.489 from Table 8, we would still expect theoretically an anisotropy of (-5,0,+5) gauss, which is considerably greater than measured experimentally. Considering the intransigence of the g and A tensors to normal analysis, and the uncertainties in determining the parameters from the experimental information used, we might expect that the calculated anisotropy values have compounded uncertainties associated with them.

II. Cyclohexadienyl-Glycolic Acid Radical

The cyclohexadienyl-glycolic acid radical appears to be formed by the addition of a hydrogen atom at the para position of a d- or l-mandelic acid molecule. This extra

hydrogen atom could come from the dissociation of a free carboxyl group into CO_2 and H, where the carboxyl group was previously removed from a d- or l-mandelic acid molecule in forming the alpha-hydroxybenzyl radical discussed above.

There are eight possible sites in the undamaged crystal, but only four sites are distinct in ESR spectra for the cyclohexadienyl-glycolic acid radical as compared to eight sites for the alpha-hydroxbenzyl radical. This would imply that the A tensors for the former radical are paired together while they are not for the latter radical. The A tensor for the CH_2 group would obviously be fixed with respect to the benzene-ring plane. As discussed previously, the d- and l-mandelic acid molecules are related by a center of symmetry so that the A tensors associated with these molecules would have the same eigenvectors if the benzene rings did not reorient. So we can conclude that the benzene rings did not significantly reorient themselves upon irradiation to form the cyclohexadienyl-glycolic acid radical. A possible scheme for the formation of the alpha-hydroxybenzyl and cyclohexadienyl-glycolic acid radicals is shown in Figure 18.

III. Summary

The ESR spectra of the radicals produced in single crystals of dl-mandelic acid by irradiation with γ-rays have been obtained and analyzed. The alpha-hydroxybenzyl radical and the cyclohexadienyl-glycolic acid radical are formed. The alpha-hydroxybenzyl radical appears to be planar, its benzene ring having reoriented during the radical formation process. The cyclohexadienyl-glycolic acid radical appears to be formed only at 77°K and the hyperfine splitting tensors of the d and l radicals are parallel.

PART I

REFERENCES

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PART I

APPENDIX

COMPUTER LISTING OF SUBROUTINES USED TO DETERMINE THE g AND A PARAMETERS FROM TENSOR VARIATIONS

APPENDIX

COMPUTER LISTING OF SUBROUTINES USED TO DETERMINE THE g AND A PARAMETERS FROM TENSOR VARIATIONS

```
      SUBROUTINE MINN
      DIMENSION XX(10),LPOS(10),SDCOS(10),IVECT(10)
      COMMON/GRAD/IGRAD,GRAD,GCOS(1)
      COMMON/XBEG/XBEG(1)/SCALE/SCALE(1)/LOCATE/V,X(1)
      COMMON/PARAGEN/NDIM,KIN,KOUT,DIST,DISTMX,VM
      COMMON/MINN/KDERV,NVDIM,NGRAD
      COMMON/TIME/TIMELIM,TBEG,TEND,ANOW,IMP,IPP,IVP,IXP
      COMMON/TITLE/ITITLE(9),NDATE(3)
C THIS SUBROUTINE IS A GENERAL ROUTINE FOR LOCATING THE MINIMUM OF A
C FUNCTION OF ANY NUMBER OF PARAMETERS. ITS BASIC METHOD IS TO USE THE
C SUBROUTINE PARAGEN WHICH WILL SEARCH FOR A MINIMUM IN ANY GIVEN
C DIRECTION BY FITTING THE CURVE TO A PARABOLA. THE MAIN PROGRAM
C CONSISTS OF METHODS OF DETERMINING IN WHICH DIRECTION PARAGEN SHOULD
C SEARCH.
C THIS PROGRAM REQUIRES: PARAGEN,VALUE,TIME,NORMGRD,CALNDER.
C LABELLED COMMONS USED: /GRAD/,/XBEG/,/LOCATE/,/SCALE/,/PARAGEN/,/MINN/
C ,/TIME/,/TITLE/.
C PUT THE ROUTINE-DETERMINING INSTRUCTIONS IN CENTRAL EVALUATION CENTER.
C  DIST IS THE LENGTH OF A NORMAL STEP.
C  KDERV = (0,1) WHEN THE SUBROUTINE VALUE (DOES NOT,DOES) CALCULATE
C    THE GRADIENT COMPONENTS.
C  LPOS(NVDIM) TELLS WHICH OF THE DIMENSION NUMBERS 1,2,....,NDIM ARE TO
C    BE VARIED.
C  NDIM IS THE NUMBER OF PARAMETERS IN THE SUBROUTINE VALUE.
C  NGRAD IS THE NUMBER OF TIMES THE GRADIENT METHOD IS USED BEFORE THE
C    PROGRAM USES THE UNIFORM-BASIC-DIRECTIONS ROUTINE.
C  NVDIM IS THE NUMBER OF THE NDIM PARAMETERS WHICH ARE TO BE VARIED.
C  SCALE(NDIM) ARE THE SCALING FACTORS TO BE USED IN THE EQUATION IN
C    SUBROUTINE VALUE: XB(I)=XBEG(I)+SCALE(I)*XA(I), WHERE XA IS BROUGHT
C    IN BY MINN AND VALUE USES THE VARIABLES XB.
C  TIMELIM IS THE NUMBER OF CENTRAL-MEMORY SECONDS FOR THE JOB.
C  TBEG,TEND ARE THE NUMBERS OF SECONDS OF HIGH-OUTPUT FROM THE
C    BEGINNING OR END OF THE PROGRAM.
C  XBEG(NDIM) ARE THE BEGINNING VALUES OF THE NDIM COMPONENTS OF X.
C STOP NUMBERS USED: 101,102,103,104,105,106,107.
C DIMENSIONIZE XX,LPOS,SDCOS,IVECT, AS (NZ) WHERE NZ.GE.NDIM.
 1000 FORMAT(1H1,27X,8A10,T124,12,1X,1A3,* 19*,12,//)
 1001 FORMAT(T50,*.... MINIMIZATION OF A FUNCTION ....*,//
     A    T42,*NDIM,THE NUMBER OF VARIABLES:*,I14,//
     B    T18,*NVDIM,THE NUMBER OF VARIABLES WHICH ARE TO BE VARIED:*
     C I14,//,   T32,*LPOS,THE VARIABLE NUMBERS TO BE VARIED:*,10I4)
 1002 FORMAT( /, T5,*KDERV=(0,1),(NO,YES),DOES SUBROUTINE VALUE CALCULAT
     AE THE GRADIENT:*,1A4   //          T10,*NGRAD,NUMBER OF TIMES THAT T
     BHE GRADIENT ROUTINE WILL BE USED:*,I14,///
     C T44,*XBEG,THE BEGINNING VALUES OF THE PARAMETERS ARE:*//(T23,6G15
     D.9,/))
 1003 FORMAT(/, T33,*SCALE,THE SCALING FACTOR IN THE EQUATION-XB(I)=XBEG
     1(I)+XA(I)*,1H*,*SCALE(I) ARE:*, //, (T23,6G15.9,/))
 1004 FORMAT( /,  T43,*DIST,THE DISTANCE OF A NORMAL STEP IS:*,1G15.9,/
     A/,  T40,*DISTMX,THE MAXIMUM DISTANCE OF A STEP IS:*,1G15.9,//
     B  T39,*TIMELIM,THE TIME LIMIT FOR THE PROGRAM IS:*,1G15.9,//
     C  T6,*TBEG,THE NUMBER OF SECONDS OF HIGH-OUTPUT FROM BEGINNING OF
     DTHE PROGRAM IS:*,1G15.9   //,      T8,*TEND,THE NUMBER OF SECONDS O
     EF HIGH-OUTPUT FROM THE END OF THE PROGRAM IS:*,1G15.9,//,
     F1X,27(5H   .  ),/)
```

```
 1185 FORMAT(/,2X,*1185-ANOW,VM =*,1G15.9,T115,1G15.9)
      INDEX=0 $ IRED=0 $ IYN=4H  NO
      IF(KDERV.EQ.1) IYN=4H YES
      DISTMX=20.0*DIST
      CALL CALNDR(NDATE)
   ... INITIALIZE LPOS
      ITT=0
      DO 10 I=1,NDIM
      IF(SCALE(I).LE.0.0) GO TO 10
      ITT=ITT+1 $ LPOS(ITT)=I
   10 CONTINUE
      PRINT 1000,ITITLE,NDATE
      PRINT 1001,NDIM,NVDIM,(LPOS(L),L=1,NVDIM)
      PRINT 1002,IYN,NGRAD,(XBEG(L),L=1,NDIM)
      PRINT 1003,(SCALE(L),L=1,NDIM)
      PRINT 1004,DIST,DISTMX,TIMELIM,TBEG,TEND
C ..... CHECK FOR BAD PARAMETERS ....
      IF(NDIM.LT.1.OR.NDIM.GT.10) STOP 101
      IF(NVDIM.LT.1.OR.NVDIM.GT.10.OR.NVDIM.NE.ITT) STOP 102
      IF(DIST.LT.1.0E-3.OR.DIST.GT.100.0) STOP 103
      IF(NGRAD.LT.0) STOP 104
      IF(TIMELIM.LT.0.0.OR.TIMELIM.GT.500.0) STOP 105
      IF(TBEG.LT.0.0.OR.TBEG.GT.500.0) STOP 106
      IF(TEND.LT.0.0.OR.TEND.GT.500.0) STOP 107
      CALL TMINIT
C ... INITIALIZE THE X VECTOR ...
      DO 2 I=1,NDIM
    2 X(I)=0.0
      IGRAD=0
70001 CALL VALUE(X,V)
      GO TO 300
C ..... GRADIENT METHOD .....
   50 CONTINUE
60001 CALL GRADNT(LPOS)
80001 CALL PARAGEN(XX)
      IRED=IRED+1
      IF((KOUT.AND.1B).NE.1B) IRED=0
      IF(IRED.LT.2) GO TO 52
      IRED=0 $ DIST=DIST/2.0 $ DISTMX=20.0*DIST
   52 DO 54 I=1,NDIM
   54 X(I)=XX(I)
      V=VM
      GO TO 300
C .... UNIFORM BASIC-DIRECTIONS ROUTINE ...
  160 KIN=0
      DO 195 NONES=1,NVDIM
      REN=1.0/SQRT(FLOAT(NONES))
      DO 162 IZ=1,NONES
  162 IVECT(IZ)=NONES+1-IZ
      GO TO 172
  164 IOBJ=1 $ IEND=NVDIM
  166 IF(IVECT(IOBJ).LT.IEND) GO TO 168
      IF(IOBJ.GE.NONES) GO TO 195
      IOBJ=IOBJ+1 $ IEND=IEND-1 $ GO TO 166
  168 IVECT(IOBJ)=IVECT(IOBJ)+1
      IF(IOBJ.EQ.1) GO TO 172
      IOBJ1=IOBJ-1 $ ISTAND=IVECT(IOBJ)+IOBJ
      DO 170 JN=1,IOBJ1
  170 IVECT(JN)=ISTAND-JN
  172 DO 173 JN=1,NDIM
  173 DCOS(JN)=0.0
  175 NONES1=NONES-1 $ IZ=IVECT(NONES) $ DCOS(LPOS(IZ))=REN
      JIND=SHIFT(1B,NONES1)
      DO 190 I=1,JIND
      II=I-1 $ IF(NONES1.EQ.0) GO TO 80002
      DO 180 IK=1,NONES1
      AL=REN $ IF((II.A.1B).EQ.1B) AL=-REN
      IZ=IVECT(IK) $ DCOS(LPOS(IZ))=AL
  180 II=II/2
80002 CALL PARAGEN(XX)
```

```
      PRINT 1195,ANOW,VM
      DO 186 JY=1,NDIM
  186 X(JY)=XX(JY)
      V=VM $ CALL TIME
  190 CONTINUE
      GO TO 164
  195 CONTINUE
C ......  CENTRAL EVALUATION CENTER ....
  300 INDEX=INDEX+1
      IF(INDEX-NGRAD) 50,50,160
      END



      SUBROUTINE TIME
      COMMON/TIME/TIMELIM,TBEG,TEND,ANOW,IMP,IPP,IVP,IXP
      GO TO (10,20,30) IABC
   10 ANOW=SECOND(A) $ DIF1=ANOW-BEG
      IF(DIF1.LT.TBEG) RETURN
      IABC=2 $ IMP=0 $ IPP=-1 $ IVP=0 $ RETURN
   20 ANOW=SECOND(A) $ DIF2=TIMELIM-ANOW
      IF(DIF2.GT.TEND) RETURN
      IABC=3 $ IMP=1 $ IPP=1 $ IVP=1 $ RETURN
      ENTRY TMINIT
      IABC=1 $ IMP=1 $ IPP=1 $ IVP=1 $ BEG=SECOND(A)
   30 RETURN
      END



      SUBROUTINE GRADNT(LPOS)
      COMMON/LOCATE/V,X(1)/GRAD/IGRAD,GRAD,DCOS(1)
      COMMON/PARAGEN/NDIM,KIN,KOUT,DIST,DISTMX,VM
      COMMON/MINN/KDERV,NVDIM,NGRAD
      DIMENSION LPOS(10),XX(10),SDCOS(10)
C ... THIS SUBROUTINE CALCULATES THE NORMALIZED GRADIENT OF A FUNCTION O
C OTHER WORDS, THE UNIT VECTOR POINTING IN THE DIRECTION OF STEEPEST ASC
C REQUIRES LABELLED COMMON: /LOCATE/,/GRAD/,/MINN/,/PARAGEN/.
C DCOS IS A VECTOR CONTAINING THE RESULTANT COMPONENTS OF THE NORMALIZED
C GRADIENT OR,IN OTHER WORDS, THE DIRECTION COSINES OF THE GRADIENT.
C GRAD IS THE MAGNITUDE OF THE GRADIENT
C NDIM IS THE NUMBER OF DIMENSIONS IN THE SPACE OF THE FUNCTION
C X IS A VECTOR CONTAINING THE INITIAL COORDINATES OF THE FUNCTION
C V IS THE VALUE OF THE FUNCTION AT THE INITIAL COORDINATES
C ..... DIMENSIONIZE: LPOS(NZ),XX(NZ),SDCOS(NZ) WHERE NZ.GE.NDIM
      IF(NDIM.LE.0.OR.NVDIM.LE.0) GO TO 91
      IF(KDERV.EQ.1) GO TO 51
      IGRAD=0 $ GRAD=0.0 $ DERSTEP=0.01*DIST
      DO 10 I=1,NDIM
      DCOS(I)=0.0
   10 XX(I)=X(I)
      DO 20 I=1,NVDIM
      II=LPOS(I)
      XX(II)=X(II)+DERSTEP
70001 CALL VALUE(XX,VV)
      XX(II)=X(II)
      DZ = (VV-V)/DERSTEP
      DCOS(II)=DZ
   20 GRAD=GRAD+DZ*DZ
      GRAD=SQRT(GRAD)
      IF(GRAD.EQ.0.0) GO TO 91
      DO 30 I=1,NDIM
   30 DCOS(I)=DCOS(I)/GRAD
      RETURN
   51 IGRAD=1
70002 CALL VALUE(X,V)
      DO 52 I=1,NDIM
      SDCOS(I)=DCOS(I)
   52 DCOS(I)=0.0
      DO 54 I=1,NVDIM
```

```
   54 DCOS(LPOS(I))=SDCOS(I)
C ..... RENORMALIZE THE DCOS VECTOR ...
      IGRAD=0 $ ZZ=0.0
      DO 56 I=1,NDIM
   56 ZZ=ZZ+DCOS(I)**2
      ZZ=SQRT(ZZ)
      IF(ZZ.EQ.0.0) GO TO 91
      DO 58 I=1,NDIM
   58 DCOS(I)=DCOS(I)/ZZ
      RETURN
   91 PRINT 191,NDIM,NVDIM,KDERV,IGRAD,GRAD,ZZ,DIST,DERSTEP,I,II,V,VV,DZ
     1,(X(L),L=1,NDIM),(LPOS(L),L=1,NVDIM)
  191 FORMAT(//,* ERROR IN GRADNT-NDIM,NVDIM,KDERV,IGRAD,GRAD,ZZ = *,
     A 4I5,2X,2G15.9,//, T16,*DIST,DERSTEP,I,II,V,VV,DZ = *, 2G15.9,2X,
     B2I5,2X,3G15.9,//,T16,*(X(L),L=1,NDIM),(LPOS(L),L=1,NVDIM) = *,
     C (T56,4G15.9,/))
      STOP 246
      END



      SUBROUTINE PARAGEN(UU)
      COMMON/GRAD/IGRAD,GRAD,DCOS(1)/LOCATE/V,X(1)
      COMMON/PARAGEN/NDIM,KIN,KOUT,DIST,DISTMX,VM
      COMMON/TIME/TIMELIM,TREG,TEND,ANOW,IMP,IPP,IVP,IXP
      DIMENSION STEP(10),XX(10),YY(10),ZZ(10),UU(10)
C     W.G.WALLER - CHEM DEP, MICH STATE U:  9 JUL 1972 - 175 CARDS
C REQUIRES LABELLED COMMON: /TIME/,/LOCATE/,/GRAD/,/PARAGEN/.
C REQUIRES SUBROUTINE VALUE.
C INPUT: X,V,DCOS,DIST,NDIM,DISTMX,KIN.  OUTPUT: KOUT,UU,VM
C PARAGEN IS TO BE USED IN A PROGRAM THAT SEARCHES FOR THE MINIMUM OF A
C FUNCTION OF NDIM VARIABLES. THE FUNCTION ITSELF IS WRITTEN AS THE
C SUBROUTINE VALUE(XA,ANS), WHERE XA(NDIM) ARE THE VARIABLES AND ANS IS
C THE FUNCTIONAL VALUE. PARAGEN IS GIVEN A STARTING SET OF PARAMETERS IN
C THE NDIM DIMENSIONAL SPACE AND A NORMALIZED VECTOR WHICH MAY POINT
C ALONG THE GRADIENT. PARAGEN BEGINS BY TAKING A STEP IN THE OPPOSITE
C DIRECTION OF THE VECTOR. IT THEN TAKES A 2ND STEP AND, IDEALLY, FITS
C THE 3 POINTS TO A PARABOLA. IT STEPS AT THE BOTTOM OF THE PARABOLA AND
C RETURNS THE VALUE OF THE FUNCTION. PARAGEN IS SET UP TO TAKE CARE OF
C ALMOST ANY CONCEIVABLE SHAPE OF CURVE ALONG WHICH IT WALKS. IT WILL
C ONLY RETURN A NEW POSITION IN THE NDIM DIMENSIONAL SPACE AND A NEW
C FUNCTIONAL VALUE IF IT IS LESS THAN THE FUNCTIONAL VALUE GIVEN TO IT.
C IF IT FINDS ITSELF ON A PERFECTLY STRAIGHT LINE, IT WILL PRINT EVERY-
C THING AND STOP.
C  X(NDIM) ARE THE VALUES GIVING THE INITIAL POSITION IN THE NDIM
C    DIMENSIONAL SPACE.
C  V IS THE INITIAL VALUE OF THE FUNCTION AT THE INITIAL POSITION.
C  DCOS(NDIM) ARE THE VALUES OF THE NORMALIZED VECTOR ALONG WHICH THE
C    SUBROUTINE PARAGEN WILL SEARCH FOR A MINIMUM.
C  DIST IS THE LENGTH OF THE STEP THAT PARAGEN SHOULD TAKE.
C  NDIM IS THE NUMBER OF VARIABLES THAT DEFINE THE FUNCTION.
C  DISTMX IS THE MAXIMUM REASONABLE DISTANCE TO BE TRAVELLED IN 1 STEP.
C  KKIN = (1,0) IF THE VECTOR DCOS(NDIM) (DOES,DOES NOT) POINT ALONG THE
C    POSITIVE GRADIENT OF THE FUNCTION.
C  KOUT IS A FLAG INTEGER WHICH IS 0 UNLESS PARAGEN USES SPECIAL
C    ROUTINES. BIT POSITIONS-1,2,3,4,5,6 ARE SET EQUAL TO 1 IF PARAGEN-
C    (1),TURNS AROUND,(2),FAILS AT FINAL CHECK,OR GOES TO THE (3),MIDDLE
C    ,(4),DOUBLE-VALLEY,(5),HILL-WALK, OR (6),CUT-OFF ROUTINES.
C  UU(NDIM) REPRESENTS THE FINAL MINIMUM POSITION ALONG THE VECTOR DCOS.
C  VM IS THE FINAL VALUE OF THE FUNCTION AT POSITION UU.
C PARAGEN USES ONLY THE VARABLE IPP IN THE LABELLED COMMON /TIME/.
C  IPP=(0,1) WHEN (NOTHING,EVERTHING IS TO BE PRINTED. IF IPP=ANOTHER
C    NUMBER, THEN ONLY FORMATS 2041,2110,2120,2502,2600 ARE PRINTED.
C DIMENSIONIZE: STEP,XX,YY,ZZ,UU AS (NZ) WHERE NZ IS GREATER THAN OR
C EQUAL TO THE LARGEST VALUE OF NDIM TO BE USED.
 2001 FORMAT(/,T10,*..... ENTERING PARAGEN: DIST = *,1G16.9,/,(T34,*DCOS
     1 = *,6G16.9,/))
 2010 FORMAT(* PARAGEN-V1,V2,XX,YY = *,2G15.9,/,(T9,5G15.9,/))
 2040 FORMAT(/,T20,*... NO LOWER VALUE FOUND: ITRY,V1,V2,V3,VM = *,1I2,
     12X,4G16.9,/)
```

```
 2041 FORMAT(/,T10,*$$$..... AFTER 4 TRIES AND USING A STEP SIZE OF *,
     1 1G16.9, *, NO LOWER VALUES WERE FOUND ..... LEAVING PARAGEN .....$
     2$$*,/)
 2042 FORMAT(/,T30,*... LEAVING PARAGEN: V1,V2,V3,VM = *,4G16.9,/)
 2100 FORMAT(/,* MIDDLE,PARAGEN2100-IDIV,DSTT,V1,V2,XX,YY,STEP = *,I5,
     1 2X,3G15.9,/,(T14,5G15.9,/))
 2110 FORMAT(//,T26,*... DOUBLE VALLEY-PARAGEN2110-V1,V2,V3,XX,YY,ZZ = *
     1 ,3G15.9,/,(T4,5G15.9,/))
 2120 FORMAT(/,20X,*........ FAILURE AT MIDDLE ROUTINE ......*,/)
 2200 FORMAT(/* HILLWALK-PARAGEN2200-ISTEP,V1,V2,V3,XX,YY,ZZ = *,I5,2X,
     1 3G15.9,/,(T19,5G15.9,/))
 2502 FORMAT(T5,*... CUTOFF-PARAGEN2502-XSUM = *,1G16.9)
 2600 FORMAT( //,T25,*...PARAGEN2600-DIVIDER IS ZERO, SO PARAGEN STOPS H
     1 ERE: V1,V2,V3,VM,DSTT,XX,YY,ZZ,UU,DCOS = *,/,(T8,5G15.9,/))
      ISTEP=0 $ ITRY=0 $ KOUT=0B
      IF(IPP.EQ.1) PRINT 2001,DIST,(DCOS(L),L=1,NDIM)
      DSTT=DIST
    2 V1=V
      DO 3 I=1,NDIM
    3 XX(I)=X(I)
    5 DO 10 I=1,NDIM
      STEP(I)=DSTT*DCOS(I)
   10 YY(I)=XX(I)-STEP(I)
70001 CALL VALUE(YY,V2)
      IF(V2.LT.V1) 16,115
  115 IF(KIN.EQ.1) GO TO 100
C.. TURN-AROUND..
   12 DO 13 I=1,NDIM
      VT=XX(I) $ XX(I)=YY(I) $ STEP(I)=-STEP(I)
   13 YY(I)=VT
      VT=V1 $ V1=V2 $ V2=VT $ DSTT=-DSTT $ KOUT=KOUT.OR.1B
   16 DO 30 I=1,NDIM
   30 ZZ(I)=YY(I)-STEP(I)
70002 CALL VALUE(ZZ,V3)
      DIVIDER = V1-V2-V2+V3
      IF(DIVIDER) 200,600,37
   37 DELTA = 0.5*DSTT*(3.0*V1-4.0*V2+V3)/DIVIDER
      IF(ABS(DELTA).GT.DISTMX) GO TO 500
   38 DO 40 I=1,NDIM
   40 UU(I)=XX(I)-DELTA*DCOS(I)
70003 CALL VALUE(UU,VM)
C..... FINAL CHECK..
      VMIN=AMIN1(V2,V3,VM)
      IF(VMIN.LT.V) GO TO 42
      ITRY=ITRY+1 $ KOUT=KOUT.OR.2B
      IF(IPP.EQ.1) PRINT 2040,ITRY,V1,V2,V3,VM
      IF(ITRY.GE.4) GO TO 41
      DSTT = -0.2*DSTT
      GO TO 2
   41 IF(IPP.NE.0) PRINT 2041,DSTT
   42 IF(IPP.EQ.1) PRINT 2042,V1,V2,V3,VM
      IF(VMIN.EQ.VM) RETURN
      IF(VMIN.EQ.V2) GO TO 55
      DO 50 I=1,NDIM
   50 UU(I)=ZZ(I)
      VM=V3 $ RETURN
   55 DO 60 I=1,NDIM
   60 UU(I)=YY(I)
      VM=V2 $ RETURN
C ... MIDDLE ROUTINE ...
  100 IDIV=0 $ KOUT=KOUT.OR.4B
      IF(IPP.EQ.1) PRINT 2100,IDIV,DSTT,V1,V2,(XX(L),L=1,NDIM),(YY(L),L=
     1 1,NDIM),(STEP(L),L=1,NDIM)
  105 V3=V2 $ DSTT=DSTT/2.0 $ IDIV=IDIV+1
      DO 110 I=1,NDIM
      STEP(I)=STEP(I)/2.0 $ ZZ(I)=YY(I)
  110 YY(I)=XX(I)-STEP(I)
70004 CALL VALUE(YY,V2)
      IF(V2.LT.V3) GO TO 120
C ..... DOUBLE-VALLEY WARNING .....
```

```
      KOUT=KOUT.OR.10B
      IF(IPP.NE.0) PRINT 2110,V1,V2,V3,(XX(L),L=1,NDIM),(YY(L),L=1,NDIM)
     1,(ZZ(L),L=1,NDIM)
  120 IF(V2.LT.V1) GO TO 37
      IF(IDIV.LT.3) GO TO 105
      IF(IPP.NE.0) PRINT 2120
      GO TO 12
C  ..... HILL-WALK ROUTINE..
  200 ISTEP=ISTEP+1
      IF(IPP.EQ.1) PRINT 2200,ISTEP,V1,V2,V3,(XX(L),L=1,NDIM),(YY(L),L=1
     1,NDIM),(ZZ(L),L=1,NDIM)
      IF(MOD(ISTEP,3).EQ.0) GO TO 210
      DO 205 I=1,NDIM
      XX(I)=YY(I)
  205 YY(I)=ZZ(I)
      V1=V2 $ V2=V3 $ KOUT=KOUT.OR.20B $ GO TO 16
  210 DO 220 I=1,NDIM
  220 XX(I)=ZZ(I)
      V1=V3 $ DSTT=DSTT+DSTT $ GO TO 5
C ... CUTOFF ROUTINE ...
  500 KOUT=KOUT.OR.40B
      VMIN=AMIN1(V1,V2,V3)
      IF(VMIN.EQ.V3) GO TO 502
      IF(VMIN.EQ.V1) GO TO 504
      DO 501 I=1,NDIM
  501 XX(I)=YY(I)
      GO TO 504
  502 DO 503 I=1,NDIM
  503 XX(I)=ZZ(I)
  504 IGO=1 $ XNUM=ABS(DELTA/DISTMX) $ V1=V3
      IF(IPP.NE.0) PRINT 2502,XNUM
      IF(XNUM.GT.3.0) GO TO 506
      DST=DELTA/2.0 $ NTIME=2 $ GO TO 520
  506 IF(XNUM.GT.9) GO TO 508
      DST=DELTA/3.0 $ NTIME=3 $ GO TO 520
  508 DST=SIGN(DISTMX,DELTA) $ NTIME=2 $ IGO=2 $ GO TO 520
  509 NTIME = IFIX(SQRT(XNUM-2.0))
      DST=DELTA/(FLOAT(NTIME)) $ IGO=1 $ GO TO 520
  520 DO 525 I=1,NDIM
  525 STEP(I)=DST*DCOS(I)
      DO 540 J=1,NTIME
      DO 530 I=1,NDIM
  530 YY(I)=XX(I)-STEP(I)
70005 CALL VALUE(YY,V2)
      IF(V2.GT.V1) GO TO 542
      DO 533 IA=1,NDIM
  533 XX(IA)=YY(IA)
      V1=V2
  540 CONTINUE
      GO TO (542,509) IGO
  542 DSTT=SIGN(DIST,DSTT) $ GO TO 5
C .... IF DIVIDER IS ZERO, EVERYTHING IS PRINTED AND PARAGEN STOPS.
  600 PRINT 2600,V1,V2,V3,VM,DSTT,(XX(L),L=1,NDIM),(YY(L),L=1,NDIM),(ZZ
     1(L),L=1,NDIM),(UU(L),L=1,NDIM),(DCOS(L),L=1,NDIM)
      STOP 600
      END



      SUBROUTINE VALUE(XA,ANS)
      COMMON/VALUE/QA,QG,XMENT(3),GMENT(3),G(3)
      COMMON/XBEG/XBEG(6)/SCALE/SCALE(6)
      COMMON/GRAD/IGRAD,GRAD,DCOS(6)
      COMMON/TIME/TIMELIM,TBEG,TEND,ANOW,IMP,IPP,IVP,IXP
      DIMENSION DFANG(3),DFGVAL(3),GX(2),R(3,3),XA(6),XB(6),DDFANG(6,3),
     1DDFGVAL(6,3),DGX(2),DR(3,3),UG(3),DXB(6),N(3),SAVE(2,3)
      DATA RD/57.2957795131/
C REQUIRES LABELLED COMMON: /VALUE/,/XBEG/,/SCALE/,/GRAD/,/TIME/.
C ALL VALUES IN THE LABELLED COMMONS MUST BE PREVIOUSLY INITIALIZED
C EXCEPT FOR GRAD AND DCOS(6) IN /GRAD/.
```

```
C NO OTHER SUBROUTINES ARE REQUIRED.
C INPUT: XA(6).   OUTPUT: ANS.
C STOP NUMBERS USED: 1234.
C THIS SUBROUTINE IS TO BE USED WITH A 6 PARAMETER MINIMIZATION PROGRAM
C TO DETERMINE THE PRINCIPLE G-VALUES AND THEIR DIRECTION COSINES FROM 3
C ISOFREQUENCY PLOTS. IT DETERMINES HOW WELL THE THEORETICAL CURVES
C PRODUCED FROM THE INPUT PARAMETERS FIT THE EXPERIMENTAL ISOFREQUENCY
C PLOTS. IT ALSO DETERMINES THE GRADIENT OF THAT VALUE. THE DIRECTION
C COSINES OF THE GRADIENT ARE IN DCOS(6) AND GRAD CONTAINS THE MAGNITUDE
C OF THE GRADIENT.
C  IGRAD=(0,1) WILL THE GRADIENT BE CALCULATED: (NO,YES).
C  XB(6) VALUES ARE GOTTEN FROM SCALING AND REPOSITIONING THE INPUT
C    XA(6) VALUES.  A,B,C=XB(1,2,3) ARE 3 EULER ANGLES THAT ARE USED TO
C    PRODUCE A ROTATION MATRIX R(3,3).
C  G(3) IS A VECTOR CONTAINING THE 3 PRINCIPLE G-VALUES.
C  XB(4,5,6) ARE THE 3 VARIABLE G-VALUE PARAMETERS. THE 3 ELEMENTS OF
C    G(3) ARE EQUATED TO XB(4,5,6).
C  R(3,3) IS THE UNITARY MATRIX THAT IS PRODUCED FROM A,B,C.
C  ANS IS THE RESULTANT ERROR ASSOCIATED WITH THE INPUT PARAMETERS.
C  QA IS THE STANDARD DEVIATION IN THE ANGLE WHERE G-MAXIMUM OCCURS.
C  QG IS THE STANDARD DEVIATION  OF THE G-VALUE RANGE FROM G-MAXIMUM TO
C    G-MINIMUM.
C  XMENT IS A VECTOR CONTAINING THE EXPERIMENTAL G-MAX ANGLES FOR THE 3
C    PLANES OF ROTATION.
C  GMENT IS A VECTOR CONTAINING THE EXPERIMENTAL G-VALUE RANGES FOR THE
C    3 PLANES OF ROTATION.
  998 FORMAT(* VALUE=998:GRAD,DCOS = *,7G15.9)
  999 FORMAT(* VALUE=999,A,B,C,G,DEANG,DEGVAL,ERANG,ERGVAL,ANS =*,//,
     A2X,6(G15.9,2X),//,2X,6(G15.9,2X),//,70X,3(G15.9,2X))
54321 FORMAT(* ERROR IN VALUE:*,/,(T10,5G15.9,/))
      DO 3 I=1,6
    3 XB(I)=XREG(I)+XA(I)*SCALE(I)
      A=XB(1) $ B=XB(2) $ C=XB(3) $ G(1)=XB(4) $ G(2)=XB(5) $ G(3)=XB(6)
      CA=COS(A) $ SA=SIN(A) $ CB=COS(B) $SB=SIN(B) $CC=COS(C) $SC=SIN(C)
      R(1,1) = CA*CB*CC-SA*SC
      R(1,2) = SA*CB*CC+CA*SC
      R(1,3) =   -SB*CC
      R(2,1) =-CA*CB*SC-SA*CC
      R(2,2) =-SA*CB*SC+CA*CC
      R(2,3) =    SB*SC
      R(3,1) = CA*SB
      R(3,2) = SA*SB
      R(3,3) =    CB
C ..... UNITARY CHECK ...
      ERROR=0.0
       DO 10 I=1,3 $ DO 10 J=1,3
      T = R(I,1)*R(J,1)+R(I,2)*R(J,2)+R(I,3)*R(J,3)
      IF(I.EQ.J) T=T-1.0
   10 ERROR=ERROR+ABS(T)
      IF(ERROR.GT.1.0E-7) GO TO 12345
      N(1)=1 $ N(2)=2 $ N(3)=3
      DO 222 IP=1,3
      NZ=N(1) $ N(1)=N(2) $ N(2)=N(3)$ N(3)=NZ $ F1=0.0 $ F2=0.0
      DO 12 J=1,3
      F1=F1+G(N(J))**2*R(N(J),N(1))*R(N(J),N(2))
   12 F2=F2+G(N(J))**2*(R(N(J),N(1))**2-R(N(J),N(2))**2)
      F2=F2/2.0
      X = (ATAN(F1/F2))/2.0 $ CX=COS(X) $ SX=SIN(X)
      DO 20 II=1,2
      GX(II)=0.0
      DO 18 J=1,3
      SAVE(II,J) =   G(N(J))*(R(N(J),N(1))*CX+R(N(J),N(2))*SX)
   18 GX(II)=GX(II)+SAVE(II,J)**2
      GX(II)=SQRT(GX(II)) $ ZZ=CX $ CX=-SX $ SX=ZZ
   20 CONTINUE
      CX=-CX $ SX=-SX,
      XD = X*RD $ IREV=0
      IF(GX(1).GE.GX(2)) GO TO 21
      XD = XD-SIGN(90.0,XD) $ IREV=1
      ZZ = GX(1) $ GX(1) = GX(2) $ GX(2) = ZZ
```

```
   21 DFANG(IP)=ABS(XD)-XMENT(IP) $ DFGVAL(IP)=GX(1)-GX(2)-GMENT(IP)
      IF(IGRAD.EQ.0) GO TO 222
C ... CALCULATE GRADIENT
      DO 30 I=1,6
   30 DXB(I)=0.0
      DO 100 IJK=1,6
      DXB(IJK)=SCALE(IJK) $ DA=DXB(1) $ DB=DXB(2) $ DC=DXB(3)
      DG(1)=DXB(4) $ DG(2)=DXB(5) $ DG(3)=DXB(6)
      DCA=-SA*DA $ DSA=CA*DA $ DCB=-SB*DB $ DSB=CB*DB $ DCC=-SC*DC
      DSC=CC*DC
      DR(1,1)=DCA*CB*CC+CA*DCB*CC+CA*CB*DCC-DSA*SC-SA*DSC
      DR(1,2)=DSA*CB*CC+SA*DCB*CC+SA*CB*DCC+DCA*SC+CA*DSC
      DR(1,3)=-DSB*CC-SB*DCC
      DR(2,1)=-DCA*CB*SC-CA*DCB*SC-CA*CB*DSC-DSA*CC-SA*DCC
      DR(2,2)=-DSA*CB*SC-SA*DCB*SC-SA*CB*DSC+DCA*CC+CA*DCC
      DR(2,3)=DSB*SC+SB*DSC
      DR(3,1)=DCA*SB+CA*DSB
      DR(3,2)=DSA*SB+SA*DSB
      DR(3,3)=DCB
      DF1=0.0 $ DF2=0.0
      DO 40 J=1,3
      GJ=G(N(J)) $ DGJ=DG(N(J)) $ RJ1=R(N(J),N(1)) $ DRJ1=DR(N(J),N(1))
      RJ2=R(N(J),N(2)) $ DRJ2=DR(N(J),N(2))
      DF1=DF1+GJ*(2.0*DGJ*RJ1*RJ2+GJ*(DRJ1*RJ2+RJ1*DRJ2))
   40 DF2=DF2+GJ*(2.0*DGJ*(RJ1**2-RJ2**2)+GJ*(2.0*RJ1*DRJ1-2.0*RJ2*DRJ2)
     D) $ DF2=DF2/2.0
      DX=((COS(2.0*X))**2/2.0)*((DF1/F2)-(F1/F2**2)*DF2)
      DCX=-SX*DX $ DSX=CX*DX
      DO 60 II=1,2
      DY=0.0
      DO 50 J=1,3
      GJ=G(N(J)) $ DGJ=DG(N(J)) $ RJ1=R(N(J),N(1)) $ DRJ1=DR(N(J),N(1))
      RJ2=R(N(J),N(2)) $ DRJ2=DR(N(J),N(2))
      DY=DY+(DGJ*(RJ1*CX+RJ2*SX)+GJ*(DRJ1*CX+RJ1*DCX+DRJ2*SX+RJ2*DSX))*
     G2.0*SAVE(II,J)
   50 CONTINUE
      DGX(II)=DY/(2.0*GX(II))
      ZZ=DCX $ DCX=-DSX $ DSX=ZZ $ ZZ=CX $ CX=-SX $ SX=ZZ
   60 CONTINUE
      CX=-CX $ SX=-SX
      DDFANG(IJK,IP)=DX*RD
      IF(XD.LT.0.0) DDFANG(IJK,IP)=-DDFANG(IJK,IP)
      DDFGVAL(IJK,IP)=DGX(1)-DGX(2)
      IF(IREV.EQ.1) DDFGVAL(IJK,IP)=-DDFGVAL(IJK,IP)
      DXB(IJK)=0.0
  100 CONTINUE
  222 CONTINUE
      ERANG=(DFANG(1)**2+DFANG(2)**2+DFANG(3)**2)/QA**2
      ERGVAL=(DFGVAL(1)**2+DFGVAL(2)**2+DFGVAL(3)**2)/QG**2
      ANS=ERANG+ERGVAL
      IF(IVP.EQ.1) PRINT 999,A,B,C,G,DFANG,DFGVAL,ERANG,ERGVAL,ANS
      IF(IGRAD.EQ.0) RETURN
      GRAD=0.0
      DO 300 I=1,6
      DERANG = 2.0*(DFANG(1)*DDFANG(I,1)+DFANG(2)*DDFANG(I,2)+
     EDFANG(3)*DDFANG(I,3))/QA**2
      DERGVAL = 2.0*(DFGVAL(1)*DDFGVAL(I,1)+DFGVAL(2)*DDFGVAL(I,2)+
     FDFGVAL(3)*DDFGVAL(I,3))/QG**2
      DCOS(I)=DERANG+DERGVAL
  300 GRAD=GRAD+DCOS(I)**2
      GRAD=SQRT(GRAD)
      DO 310 I=1,6
  310 DCOS(I)=DCOS(I)/GRAD
      IF(IVP.EQ.1) PRINT 998,GRAD,DCOS
      RETURN
12345 PRINT 54321,A,B,C,G,CA,CB,CC,SA,SB,SC,R,ERROR
      STOP 1234
      END
```

PART II

A GENERALIZATION OF METHODS FOR DETERMINING g TENSORS

INTRODUCTION

Several authors have derived procedures for determining the principal values, and the directions of the principal axes, of the g tensor from magnetic resonance data.[1-4] These involve measurements of $g=h\nu/\beta H$ at orientations provided by rotating the crystal about each of three axes. Any symmetric second-rank tensor may be evaluated by the same procedures, and examples include the zero-field splitting and hyperfine interaction tensors $\overline{\overline{D}}$ and $\overline{\overline{A}}$, respectively.[5] The necessary equations have been reported only for the cases of rotation about three orthogonal axes[1-5] and three monoclinic axes[3] and contain an overdetermination of some of the tensor elements. It was suggested that additional information in the form of rotational misalignments can also be obtained from the data and a technique for so doing in the orthorhombic case was presented.[4]

In this article a general formalism is developed which converts the inherent over-specification of tensor elements into a determination of the three rotational misalignments. It is applied to the orthorhombic and

monoclinic cases, the potentially useful case of three coplanar axes, and the general case of rotation about any three axes. The latter two cases have not been discussed previously. Since it is frequently possible to mount a crystal most precisely by choosing general or coplanar rotation axes, these latter methods should prove useful in experimental investigations. Also, the determination of the three azimuthal misalignments in each case will serve to make fullest use of data and to improve the accuracy of the derived tensors.

DATA FOR g-TENSOR DETERMINATION

Experimental

Experimentally the crystal is mounted so it may be rotated about a specific axis and ESR spectra are recorded for various orientations of the magnetic field in the plane perpendicular to that axis. The g values are plotted as a function of rotation angle θ, which is taken as positive when the crystal is rotated clockwise (or magnetic field rotated counterclockwise) as viewed from above. Three such plots for the three chosen rotation axes constitute the experimental data.

Parameterization of the Data

Depending on the quality of the plots, three levels of analysis may be employed. The first method (called the $\alpha\beta\gamma$ method below) utilizes either all the data in a curve-fitting procedure or only the g extrema with the corresponding angles θ. In the second method ($\alpha\lambda$ method), only the g extrema are used.

As will be shown below (Equation (28)), the g values for rotation about any axis must obey the equation (in the notation of reference 3)

$$g^2 = \alpha + \beta\cos 2\theta + \gamma\sin 2\theta. \qquad (1)$$

The most accurate values of the parameters α, β, γ would be obtained by a least-squares fit of the data to Equation (1). Alternatively, $\alpha\beta\gamma$ may be evaluated from the equations for the extrema:

$$\alpha = (g_+^2 + g_-^2)/2, \quad \beta = (g_+^2 - g_-^2)\cos 2\theta_+/2, \quad \gamma = (g_+^2 - g_-^2)\sin 2\theta_+/2, \qquad (2)$$

obtained by differentiation of Equation (1); g_+, g_- are the maximum and minimum g values in the given plot (or vice versa) and θ_+ is the angle corresponding to g_+; θ_+ should be taken from the best extremum.

For a rotation about any axis, each experimental spectrum is associated with an angle θ read on a protractor. The numerical values of θ then depend on the arbitrarily chosen initial placement of the crystal. The position of the crystal associated with $\theta = 0°$ is called the "experimental" initial orientation. Since $\theta' = \theta + 180°$ also satisfied Equation (1), we see that the initial conditions specified have a twofold ambiguity. In developing the theory, it is necessary to specify the orientation of the crystal in the cavity at the beginning of each rotation, i.e., the orientation of the crystal axes a, b, c when $\theta = 0°$ for each rotation is required. These are called the three "theoretical" initial orientations. The main error in orienting crystals is the azimuthal angle error,

which is the rotation error $\delta\theta$; we neglect in these calculations errors in the orientation of the vertical axis. The aximuthal angle $\delta\theta$ from the actual "experimental" to the "theoretical" initial orientation is called the starting-angle shift. The three starting-angle shifts can always be evaluated.

The data may also be analyzed using only the g extrema by employing the parameters

$$\alpha = (g_+^2 + g_-^2)/2, \qquad \lambda = |g_+^2 - g_-^2|/2. \tag{3}$$

The α, β, γ parameters are used below to solve the general, coplanar, orthorhombic, and monoclinic cases while the later two are also solved explicitly using the α, λ parameters. In addition, all cases may be treated using only the α, λ parameters by setting $\beta = \lambda$ and $\gamma = 0$ (which is equivalent to introducing an unknown starting-angle shift) and employing the $\alpha\beta\gamma$ method.

GENERAL THEORY

The value of g at a specific orientation has been shown to be given by[1]

$$g^2 = \sum_{i,j=1}^{3} W_{ij} \ell_i \ell_j \quad (W_{ij} = W_{ji}), \tag{4}$$

where ℓ_1, ℓ_2, ℓ_3 are the direction cosines of the uniform magnetic field with respect to a set of orthogonal axes 1, 2, 3 fixed with respect to the crystal. The relationship between the W and g tensors is $\overline{\overline{W}} = \overline{\overline{g}}^2$. When the symmetric tensor $\overline{\overline{W}}$ is diagonalized, the squares of the principal g values, and their direction cosines, are determined. The Jacobi method[6] is a very good way to diagonalize the matrix. The general problem is thus reduced to determining the six coefficients (matrix elements) W_{11}, W_{22}, W_{33}, W_{12}, W_{23}, W_{13}.

Nomenclature

The three experimental rotation axes, fixed with respect to the crystal, are labeled a, b, c. Along these axes are placed three rotation vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ chosen so that rotation of the magnetic field is in a right-handed

sense about the vectors. Where appropriate, the letters a, b, c are used as subscripts to the parameters α, β, γ, λ, θ_+, g_+, g_-, $\vec{S}$, $\vec{M}$ obtained from the respective rotations. A coordinate system consisting of a specific arbitrary set of three orthogonal axes labeled 1, 2, 3, also fixed with respect to the crystal, is chosen for each of the cases treated in this investigation. It must be remembered that the direction cosines obtained by diagonalizing the W matrix will be relative to the 1 2 3 coordinate system chosen.

Considerable simplification of the equations was found to result from choosing the 1 2 3 coordinate system such that rotation vector $\vec{a}$ points along the positive $\vec{3}$ axis and $\vec{b}$ lies in the $\vec{1}$ $\vec{3}$ plane at an angle ϕ from $\vec{3}$ as shown in Figure 1a. Here $\vec{1}$ $\vec{2}$ $\vec{3}$ are three orthonormal vectors in a right-handed relationship and a positive or negative sign is given to ϕ according to whether it represents a right- or left-handed screw sense rotation about $\vec{2}$ (Figure 1). The four experimental cases considered--coplanar, monoclinic, orthorhombic and general--then correspond, respectively, to the conditions (a) vector $\vec{c}$ in the $\vec{1}$ $\vec{3}$ plane, (b) vector $\vec{c}$ along $\vec{2}$, (c) vector $\vec{c}$ along $\vec{2}$ and ϕ = +90°, and (d) vector $\vec{c}$ in none of the above relationships (i.e., $\vec{c}$ points in an arbitrary direction).

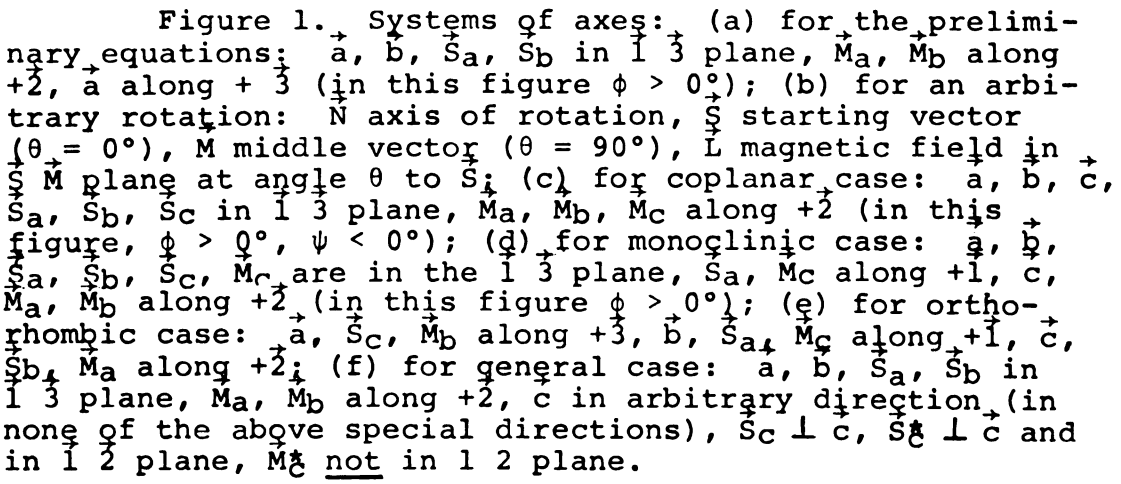

Figure 1. Systems of axes: (a) for the preliminary equations: $\vec{a}$, $\vec{b}$, $\vec{S}_a$, $\vec{S}_b$ in 1 3 plane, $\vec{M}_a$, $\vec{M}_b$ along $+\vec{2}$, $\vec{a}$ along $+\vec{3}$ (in this figure $\phi > 0°$); (b) for an arbitrary rotation: $\vec{N}$ axis of rotation, $\vec{S}$ starting vector ($\theta = 0°$), M middle vector ($\theta = 90°$), L magnetic field in $\vec{S}$ $\vec{M}$ plane at angle θ to $\vec{S}$; (c) for coplanar case: $\vec{a}$, $\vec{b}$, $\vec{c}$, $\vec{S}_a$, $\vec{S}_b$, $\vec{S}_c$ in 1 3 plane, $\vec{M}_a$, $\vec{M}_b$, $\vec{M}_c$ along $+\vec{2}$ (in this figure, $\phi > 0°$, $\psi < 0°$); (d) for monoclinic case: $\vec{a}$, $\vec{b}$, $\vec{S}_a$, $\vec{S}_b$, $\vec{S}_c$, $\vec{M}_c$ are in the 1 3 plane, $\vec{S}_a$, $\vec{M}_c$ along $+\vec{1}$, $\vec{c}$, $\vec{M}_a$, $\vec{M}_b$ along $+\vec{2}$ (in this figure $\phi > 0°$); (e) for orthorhombic case: $\vec{a}$, $\vec{S}_c$, $\vec{M}_b$ along $+\vec{3}$, $\vec{b}$, $\vec{S}_a$, $\vec{M}_c$ along $+\vec{1}$, $\vec{c}$, $\vec{S}_b$, $\vec{M}_a$ along $+\vec{2}$; (f) for general case: $\vec{a}$, $\vec{b}$, $\vec{S}_a$, $\vec{S}_b$ in 1 3 plane, $\vec{M}_a$, $\vec{M}_b$ along $+\vec{2}$, $\vec{c}$ in arbitrary direction (in none of the above special directions), $\vec{S}_c \perp \vec{c}$, $\vec{S}_c^* \perp \vec{c}$ and in 1 2 plane, $\vec{M}_c^*$ <u>not</u> in 1 2 plane.

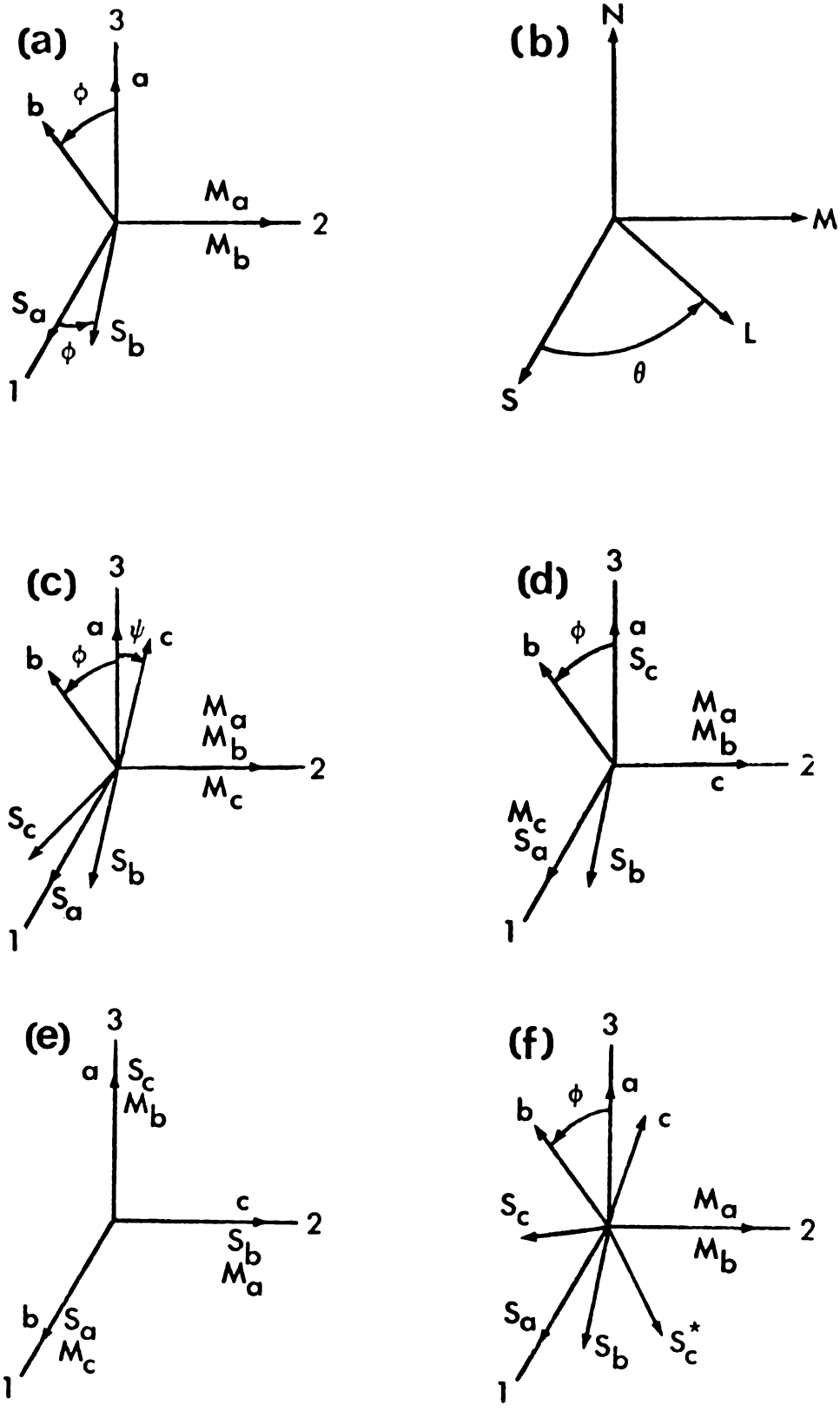
(a)
3
a
b
ϕ
M_a
M_b
2
S_a
S_b
ϕ
1
(b)
N
M
L
S
θ
(c)
3
a
ψ
c
b
ϕ
M_a
M_b
M_c
2
S_c
S_b
S_a
1
(d)
3
a
b
ϕ
S_c
M_a
M_b
2
c
M_c
S_a
S_b
1
(e)
3
a
S_c
M_b
c
2
S_b
M_a
b
S_a
M_c
1
(f)
3
a
b
ϕ
c
S_c
M_a
2
M_b
S_a
S_b
S_c^*
1

Figure 1.

General Formulation

There are nine parameters to determine the six W coefficients and the three starting-angle errors in the $\alpha\beta\gamma$ method. The nine functions $W_{11}(\alpha_a\beta_a\gamma_a\alpha_b\beta_b\gamma_b\alpha_c\beta_c\gamma_c)$, $W_{22}(...)$, $W_{33}(...)$, $W_{12}(...)$, $W_{23}(...)$, $W_{13}(...)$, $\varepsilon_1(...)$, $\varepsilon_2(...)$, and $\varepsilon_3(...)$ are set up, where the <u>values</u> of the six W functions for any set of α, β, γ values represent the approximate values of the W coefficients and the values of the three ε functions represent three measures of the magnitude of the starting-angle shifts. The parameters α, β, γ from Equation (1) are functions of the starting-angle shifts $\delta\theta_a$, $\delta\theta_b$, $\delta\theta_c$ since α, β, γ depend on the choice of the "theoretical" initial orientations. When the "true" starting-angle shifts $\delta\theta_a^t$, $\delta\theta_b^t$ and $\delta\theta_c^t$ are used, the values of α, β, γ become the "true" parameters $\alpha^t \equiv \alpha(\delta\theta_a^t,\delta\theta_b^t,\delta\theta_c^t)$, $\beta^t \equiv \beta(\delta\theta_a^t,\delta\theta_b^t,\delta\theta_c^t)$, $\gamma^t \equiv \gamma(\delta\theta_a^t,\delta\theta_b^t,\delta\theta_c^t)$, while the ε functions become zero, $\varepsilon_1(\alpha_a^t\beta_a^t\gamma_a^t\alpha_b^t\beta_b^t\gamma_b^t\alpha_c^t\beta_c^t\gamma_c^t) = \varepsilon_2(...) = \varepsilon_3(...) = 0$, and

$$W_{11}(\alpha_a^t\beta_a^t\gamma_a^t\alpha_b^t\beta_b^t\gamma_b^t\alpha_c^t\beta_c^t\gamma_c^t),\ W_{22}(...),\ \text{etc.},$$

become the "true" values of the components of the W tensor. The ε_1, ε_2, ε_3 functions are called null functions because the condition that they all be simultaneously zero is used to determine the true starting-angle shifts and thus the true α, β, γ parameters and the W tensor.

In the $\alpha\lambda$ method there are six parameters, the six W coefficients, to determine. After $\overline{\overline{W}}$ is diagonalized, the values of θ_+ with respect to any rotation and any arbitrary initial orientation may be calculated by using the formulas of Equation (29) with the relation $\theta_+ = (1/2)\tan^{-1}(\gamma/\beta)$ obtained from Equation (2). The difference between the calculated and the experimental θ_+ (each with respect to the same initial orientation chosen) is equal to the starting-angle shift for that rotation.

Determination of Starting-Angle Shifts

In this section, formulas are derived giving the dependence of α, β, γ on the starting-angle shifts $\delta\theta_a$, $\delta\theta_b$, $\delta\theta_c$ and the original α, β, γ values. The formulas are used, along with a condition on the null functions developed here, to obtain the "true" starting-angle shifts. From the latter, the "true" α, β, γ values are then obtained and the "true" components of $\overline{\overline{W}}$ computed.

If, in a certain rotation, the angle assigned to each orientation is changed by an amount $\delta\theta$ so that $\theta = \theta' + \delta\theta$, then Equation (1) becomes

$$g^2 = \alpha + \beta\cos(2\theta' + 2\delta\theta) + \gamma\sin(2\theta' + 2\delta\theta)$$

$$= \alpha + (\beta\cos2\delta\theta + \gamma\sin2\delta\theta)\cos2\theta' + (\gamma\cos2\delta\theta - \beta\sin2\delta\theta)\sin2\theta'$$

$$= \alpha' + \beta'\cos2\theta' + \gamma'\sin2\theta', \qquad (5)$$

from which, using Equations (2) and (3), we see that

$$\alpha' = \alpha, \quad \beta' = \lambda\cos\zeta, \quad \gamma' = \lambda\sin\zeta, \tag{6}$$

where $\zeta = 2\theta_+ - 2\delta\theta$. When the "true" $\delta\theta_i$ are used, we obtain the "true" values for $\alpha_i^t, \beta_i^t, \gamma_i^t$, and ζ_i^t. The values of the three null functions then become

$$\varepsilon_i^t(\alpha_a^t\beta_a^t\gamma_a^t\alpha_b^t\beta_b^t\gamma_b^t\alpha_c^t\beta_c^t\gamma_c^t) = \varepsilon_i(\alpha_a\beta_a\gamma_a\alpha_b\beta_b\gamma_b\alpha_c\beta_c\gamma_c) + \delta\varepsilon_i = 0, \tag{7a}$$

$$\delta\varepsilon_i = -\varepsilon_i \qquad (i = 1,2,3), \tag{7b}$$

where $\delta\varepsilon_i$ is defined by Equation (7a). Also, from Equations (6) we can rewrite this in terms of the variables ζ_i as

$$\varepsilon_i^t(\lambda_a\lambda_b\lambda_c, \zeta_a^t\zeta_b^t\zeta_c^t) = 0 \qquad (i = 1,2,3). \tag{8}$$

In some cases the exact solution of the three simultaneous equations (7) or (8) is prohibitively complicated. It can then be determined by an iterative procedure using simpler equations. It is, in general, more convenient to define the quantities $\Delta_i = 2\delta\theta_i$ $(i = a,b,c)$; then, to first order in Δ,

$$\begin{aligned} \delta\alpha_i &= 0 & \alpha_i' &= \alpha_i, \\ \delta\beta_i &= \gamma_i\Delta_i, & \beta_i' &= \beta_i + \delta\beta_i, \\ \delta\gamma_i &= -\beta_i\Delta_i, & \gamma_i' &= \gamma_i + \delta\gamma_i \qquad (i = a,b,c). \end{aligned} \tag{9}$$

These are substituted into Equations (7), which are then solved for Δ_a, Δ_b, Δ_c.

THEORY--DERIVATION OF FORMULAS

Preliminary Equations

A general rotation may be expressed in the following way. Let $\vec{N}$, $\vec{S}$, $\vec{M}$ be right-handed orthonormal vectors as shown in Figure 1b with $\vec{N}$ representing the axis of rotation, $\vec{S}$ the magnetic field direction at the start of the rotation and $\vec{M}$ the magnetic field direction at the "middle" of the rotation ($\theta = 90°$). Let $\vec{L}$ be a unit vector representing the direction of the magnetic field as it sweeps the $\vec{S}$ $\vec{M}$ plane in a right-handed sense about $\vec{N}$ (Figure 1b). Let θ of Equation (1) be the angle between $\vec{L}$ and $\vec{S}$ (rotating $\vec{L}$ by $+\theta$ is the same as rotating the crystal by $-\theta$), then

$$\vec{M} = \vec{N} \times \vec{S} \text{ and } \vec{L} = \vec{S}\cos\theta + \vec{M}\sin\theta. \qquad (10)$$

With respect to any axes 1, 2, 3 one has, from Equations (4) and (10),

$$\ell_i = S_i\cos\theta + M_i\sin\theta \qquad (i = 1,2,3). \qquad (11)$$

Choosing the 1 2 3 coordinate system in Figure 1a, one sees that for the rotation about the a axis, the

arbitrary initial orientation (where $\theta = 0°$) is specified to be along the $\vec{1}$ axis, so that $\vec{N}_a = \vec{3}$, $\vec{S}_a = \vec{1}$, and $\vec{M}_a = \vec{2}$. From Equation (11) one has $\ell_i = S_1\cos\theta + M_1\sin\theta = \cos\theta$, $\ell_2 = S_2\cos\theta + M_2\sin\theta = \sin\theta$ and $\ell_3 = S_3\cos\theta + M_3\sin\theta = 0$, which, when substituted into Equation (4), give

$$g^2 = W_{11}\cos^2\theta + W_{22}\sin^2\theta + 2W_{12}\cos\theta\sin\theta$$

$$= \tfrac{1}{2}(W_{11} + W_{22}) + \tfrac{1}{2}(W_{11} - W_{22})\cos 2\theta + W_{12}\sin 2\theta \qquad (12)$$

and, by comparison with Equation (1), it may be seen that

$$\alpha_a = \tfrac{1}{2}(W_{11} + W_{22}), \quad \beta_a = \tfrac{1}{2}(W_{11} - W_{22}), \quad \gamma_a = W_{12} \qquad (13)$$

and, solving for the W coefficients, one obtains

$$W_{11} = \alpha_a + \beta_a, \quad W_{22} = \alpha_a - \beta_a, \quad W_{12} = \gamma_a. \qquad (14)$$

For the rotation about axis b we specify that the initial orientation occurs when the magnetic field is in the 1 3 plane. From Figure 1a we see that $\vec{N}_b = \vec{3}\cos\phi + \vec{1}\sin\phi$, $\vec{S}_b = \vec{1}\cos\phi - \vec{3}\sin\phi$, and $\vec{M}_b = \vec{2}$. Again: $\ell_1 = \cos\phi\cos\theta$, $\ell_2 = \sin\theta$ and $\ell_3 = -\sin\phi\cos\theta$, and substituting these into Equation (4) one obtains

$$g^2 = (W_{11}\cos^2\phi + W_{33}\sin^2\phi - 2W_{13}\cos\phi\sin\phi)\cos^2\theta + (W_{22})\sin^2\theta$$

$$+ 2(W_{12}\cos\phi - W_{23}\sin\phi)\cos\theta\sin\theta. \qquad (15)$$

Since Equation (15) is an exact analogue of Equation (12), the solutions analogous to Equation (14) are written

$$W_{11}\cos^2\phi + W_{33}\sin^2\phi - 2W_{13}\cos\phi\sin\phi = \alpha_b + \beta_b, \quad (16)$$

$$W_{22} = \alpha_b - \beta_b, \quad (17)$$

$$W_{12}\cos\phi - W_{23}\sin\phi = \gamma_b. \quad (18)$$

Using Equations (14) in (18), the W_{23} coefficient may be defined as

$$W_{23} = (\gamma_a\cos\phi - \gamma_b)/\sin\phi. \quad (19)$$

Comparing Equations (14) and (17) leads to the relation

$$\alpha_b - \beta_b - \alpha_a + \beta_a = 0, \quad (20)$$

which may be used as a null function. Substituting from Equation (14) into (16) and using Equation (20) to cancel the α_b term gives

$$\sin 2\phi(W_{13}) - \sin^2\phi(W_{33} - \alpha_a) = \beta_a(1 + \cos^2\phi) - 2\beta_b. \quad (21)$$

From the six parameters α_a, β_a, γ_a, α_b, β_b, γ_b used so far, four relationships involving W_{11}, W_{22}, W_{12}, W_{23}, one relationship involving W_{13} and W_{33}, and one null relationship have been defined. The third rotation, which differs in each of the four cases, will be treated separately for each individual case below.

Case of Three Coplanar Axes

If the third rotation axis c lies in the 1 3 plane, along with the a and b axes, we have the coplanar case. Let ϕ, ψ be the angles between 3 and b, c, respectively; these have a positive or negative sign according to whether they represent a right- or left-handed screw sense about $\vec{2}$, and let the initial orientation vectors $\vec{S}_b$, $\vec{S}_c$ lie in the 1 3 plane (Figure 1c). From Equations (19)-(21), with ψ and c replacing ϕ and b, we obtain

$$W_{23} = (\gamma_a \cos\psi - \gamma_c)/\sin\psi, \tag{22}$$

$$\alpha_c - \beta_c - \alpha_a + \beta_a = 0, \tag{23}$$

$$\sin 2\psi(W_{13}) - \sin^2\psi(W_{33} - \alpha_a) = \beta_a(1 + \cos^2\psi) - 2\beta_c. \tag{24}$$

Equations (21) and (24) can now be solved to give W_{13} and W_{33}. Equations (20) and (23) provide two null functions and the third is derived from a comparison of Equation (19) with Equation (22). For the iterative solution, we apply Equations (7) and (9) to the null function ε_1 leading to

$$\delta_1 = \delta\alpha_b - \delta\beta_b - \delta\alpha_a + \delta\beta_a = 0 - \gamma_b\Delta_b - 0 + \gamma_a\Delta_a = -\varepsilon_1,$$

$$\Delta_b = (\varepsilon_1/\gamma_b) + (\gamma_a/\gamma_b)\Delta_a = B + B'\Delta_a. \tag{25}$$

Similarly, applying Equations (7) and (9) to the analogous ε_2 null function gives

$$\Delta_c = (\varepsilon_2/\gamma_c) + (\gamma_a/\gamma_c)\Delta_a = C + C'\Delta_a.$$

Again, with ε_3 and the above relationships,

$$\delta\varepsilon_3 = -\beta_a\Delta_a\sin(\psi - \phi) + \beta_b\Delta_b\sin\psi - \beta_c\Delta_c\sin\phi$$

$$= (\beta_b B\sin\psi - \beta_c C\sin\phi) - [\beta_a\sin(\psi - \phi) - \beta_b B'\sin\psi + \beta_c C'\sin\phi]\Delta_a$$

$$= -\varepsilon_3,$$

which is solved for Δ_a. These results for the approximate solution are listed in the Collected Formulas, as are some properties of the exact solution of Equation (8).

Case of Three Monoclinic Axes

If the c axis, about which the magnetic field is rotated in a right-handed sense, is perpendicular to the 1 3 plane, we have the monoclinic case. Let the c axis point along the +2axis (Figure 1d). Note, however, that if the experimental c axis actually pointed along the -2 axis, then one must change $\theta_c \rightarrow -\theta_c$ (or equivalently $\gamma_c \rightarrow -\gamma_c$) to use the formulas. The initial orientation for this rotation is selected so that the magnetic field is along the 3 axis for $\theta = 0°$ hence $\vec{N} = \vec{2}$, $\vec{S} = \vec{3}$ and $\vec{M} = \vec{1}$. Therefore, from Equation (11), $\ell_1 = \sin\theta$, $\ell_2 = 0$, $\ell_3 = \cos\theta$, and from Equation (4),

$$g^2 = W_{33}\cos^2\theta + W_{11}\sin^2\theta + 2W_{13}\sin\theta\cos\theta,$$

which is the same form as Equation (12). So, according to Equation (14),

$$W_{33} = \alpha_c + \beta_c, \quad W_{11} = \alpha_c - \beta_c, \quad W_{13} = \gamma_c. \tag{26}$$

Equations (14) and (26) are used to define W_{13}, W_{33} and the null function

$$\varepsilon_1 = \alpha_c - \beta_c - \alpha_a - \beta_a.$$

Then, equating Equations (14) and (17) gives an expression for β_a which, when substituted in ε_1, gives $\varepsilon_2 = \alpha_c - \beta_c + \beta_b - 2\alpha_a$. Substituting ε_2 and all the relations of Equation (26) in Equation (16) and dividing by two gives $\varepsilon_3 = (\alpha_b - \alpha_a) + \sin\phi(\gamma_c\cos\phi - \beta_c\sin\phi)$.

Applying Equation (7) to the three null functions gives $\delta\varepsilon_1 = -\varepsilon_1 = -\gamma_c\Delta_c - \gamma_a\Delta_a$, $\delta\varepsilon_2 = -\varepsilon_2 = -\gamma_c\Delta_c - \gamma_b\Delta_b$ and $\delta\varepsilon_3 = -\varepsilon_3 = \sin\phi(-\beta_c\Delta_c\cos\phi - \gamma_c\Delta_c\sin\phi)$. From these the Δ_i's are obtained directly for the formulas of the iterative method. The exact solution has also been obtained from Equation (8) and the formulas for the $\alpha\lambda$ method worked out.

Case of Three Orthorhombic Axes

The initial orientations are best chosen in a cyclic manner (Figure 1e), because of the high symmetry of the a, b, c axes, i.e., for rotation about a, b or c the $\theta = 0°$ orientation is chosen in the ab, bc or ca plane, respectively. The problem is then set up so that there is a cyclic relationship betweeen the three rotations. The formulas in Equation (14) for a rotation about the a axis can then be extended in a cyclic manner to the other rotations by changing the subscripts of α, β, γ, and W as

as follows: a → b → c, 11 → 22 → 33, 12 → 23 → 13. The result of this is

Rotation a	Rotation b	Rotation c
$W_{11} = \alpha_a + \beta_a$	$W_{22} = \alpha_b + \beta_b$	$W_{33} = \alpha_c + \beta_c$
$W_{22} = \alpha_a - \beta_a$	$W_{33} = \alpha_b - \beta_b$	$W_{11} = \alpha_c - \beta_c$
$W_{12} = \gamma_a$	$W_{23} = \gamma_b$	$W_{13} = \gamma_c$

(27)

The first and third rows of Equation (27) define the W coefficients. Subtracting the first row of relationships from the second row, dividing by two, and using the relation $-\beta_b - \beta_c = \alpha_c - \alpha_b$ obtained from the two formulas for W_{33} gives ε_1; ε_2, ε_3 are then obtained by cyclic permutations of ε_1.

Using Equation (9) we obtain for the iterative solution $\delta\varepsilon_1 = -\gamma_a\Delta_a = -\varepsilon_1$ so that $\Delta_a = \varepsilon_1/\gamma_a$.

For the exact solution, we have from Equations (8), $\alpha_c - \alpha_b - \lambda_a\cos\zeta_a = 0$ which is straightforwardly solved for ζ_a. The solutions for Δ_b, Δ_c, ζ_b, ζ_c are obtained from those of Δ_a and ζ_a by a cyclic permutation.

For the $\alpha\lambda$ method, it is seen from ε_1 that the "true" parameters obey the relation $\beta_a = \alpha_c - \alpha_b$, which gives $W_{11} = \alpha_a - \alpha_b + \alpha_c$ and $\gamma_a = \pm [\lambda_a^2 - (\alpha_c - \alpha_b)^2]^{1/2} = W_{12}$, and cyclically the remaining W coefficients. All the results are listed in the Collected Formulas.

General Case

If the third axis of rotation does not satisfy the conditions for any of the previous cases, we have the general case (Figure 1f). The direction of the rotation axis c (about which the magnetic field rotates in a right-handed sense) must be known, while the initial orientation need only be determined within a twofold ambiguity.

Let

$$\vec{N} = N_1\vec{1} + N_2\vec{2} + N_3\vec{3}, \quad \vec{S} = S_1\vec{1} + S_2\vec{2} + S_3\vec{3}, \quad \text{and} \quad \vec{M} = \vec{N} \times \vec{S}$$

be unit vectors representing the rotation axis, the initial orientation ($\theta = 0°$) and the $\theta = 90°$ direction, respectively. The three starting-angle errors, being a property of the data, are independent of the coordinate system chosen to solve for them; hence we are allowed to choose a more convenient system to simplify the solution. One such system is obtained by choosing a different initial unit vector $\vec{S}^*$ in the $\vec{S}$ $\vec{M}$ plane with the property that $S_3^* = 0$. Let ξ be the angle between $\vec{S}$ and $\vec{S}^*$ so that $\vec{S}^* = \vec{S}\cos\xi + \vec{M}\sin\xi$ and $\vec{M}^* = \vec{M}\cos\xi - \vec{S}\sin\xi$. Then ξ must satisfy the relation $\tan\xi = -S_3/M_3$. One such transformation that will change $\vec{S}$ and $\vec{M}$ into $\vec{S}^*$ and $\vec{M}^*$ is

$$S_1^* = (S_1M_3 - S_3M_1)/\Lambda, \quad M_1^* = (S_1S_3 + M_1M_3)/\Lambda,$$

$$S_2^* = (S_2M_3 - S_3M_2)/\Lambda, \quad M_2^* = (S_2S_3 + M_2M_3)/\Lambda,$$

$$S_3^* = 0, \quad M_3^* = \Lambda,$$

where $\Lambda = \sqrt{(S_3^2 + M_3^2)}$. Similarly the corresponding transformation between the old α_c, β_c, γ_c, λ_c and the new α_c^*, β_c^*, γ_c^*, λ_c^* parameters would be from Equations (3) and (5)

$$\alpha_c^* = \alpha_c, \qquad \lambda_c^* = \lambda_c,$$

$$\beta_c^* = \beta_c\cos(2\xi) + \gamma_c\sin(2\xi) = [\beta_c(M_3^2 - S_3^2) - 2\gamma_c M_3 S_3]/\Lambda^2,$$

$$\gamma_c^* = \gamma_c\cos(2\xi) - \beta_c\sin(2\xi) = [\gamma_c(M_3^2 - S_3^2) + 2\beta_c M_3 S_3]/\Lambda^2.$$

Substituting Equation (11) into Equation (4), remembering that $W_{ij} = W_{ji}$, and noting the analogy with Equation (12), we arrive at the result

$$\begin{aligned} g^2 &= \sum_{i,j=1}^{3} W_{ij}\ell_i\ell_j \\ &= \Big(\sum_{i,j} W_{ij}S_iS_j\Big)\cos^2\theta + \Big(\sum_{i,j} W_{ij}M_iM_j\Big)\sin^2\theta + 2\Big(\sum_{i,j} W_{ij}S_iM_j\Big)\cos\theta\sin\theta \\ &= \alpha_c + \beta_c\cos2\theta + \gamma_c\sin2\theta \end{aligned} \tag{28}$$

analogous to Equation (13), where

$$\begin{aligned} \alpha_c &= \tfrac{1}{2}\textstyle\sum_{ij} W_{ij}(S_iS_j + M_iM_j), \\ \beta_c &= \tfrac{1}{2}\textstyle\sum_{ij} W_{ij}(S_iS_j - M_iM_j), \\ \gamma_C &= \textstyle\sum_{ij} W_{ij}S_iM_j. \end{aligned} \tag{29}$$

Since Equations (28) and (29) hold for rotations about any axis, they may be used as a check on the correctness of the

W tensor by reproducing the original α, β, γ parameters. For the case with $S_3^* = 0$, Equation (29) gives

$$\alpha_c^* + \beta_c^* = W_{11}S_1^{*2} + W_{22}S_2^{*2} + 2W_{12}S_1^*S_2^*, \tag{30}$$

$$\alpha_c^* - \beta_c^* = W_{11}M_1^{*2} + W_{22}M_2^{*2} + W_{33}M_3^{*2} + 2W_{12}M_1^*M_2^* + 2W_{23}M_2^*M_3^* + 2W_{13}M_1^*M_3^*, \tag{31}$$

$$\gamma_c^* = W_{11}S_1^*M_1^* + W_{22}S_2^*M_2^* + W_{12}(S_1^*M_2^* + S_2^*M_1^*) + W_{23}S_2^*M_3^* + W_{13}S_1^*M_3^*. \tag{32}$$

With the identities $S_1^{*2} + S_2^{*2} = 1$ and $S_1^*M_1^* + S_2^*M_2^* = 0$, we use Equations (14), (19), (32), and (16) to define W_{11}, W_{22}, W_{12}, W_{23}, W_{13}, and W_{33}, respectively. By comparing Equations (14) and (17), the first null function $\varepsilon_1 = \alpha_b - \beta_b - \alpha_a + \beta_a$ is derived. Using the formulas for the W coefficients and Equation (30), the second null function

$$\varepsilon_2 = \alpha_a + \beta_a(2S_1^{*2} - 1) + 2\gamma_aS_1^*S_2^* - \alpha_c^* - \beta_c^*$$

is obtained. The third null function ε_3, listed in Table 1, follows similarly from Equation (31). Considering the approximate solution, we see that since ε_1 is the same as in the coplanar case, Δ_b is given by Equation (25). Using ε_2 in Equations (7) and (9) leads to the relationship

$$\Delta_c = (\varepsilon_2/\gamma_c^*) + \left\{\frac{\gamma_a(2S_1^{*2} - 1) - 2\beta_aS_1^*S_2^*}{\gamma_c^*}\right\}\Delta_a = C + C'\Delta_a.$$

In order to use the third null function ε_3 it is necessary to obtain δW_{23}, δW_{13}, and δW_{33}; these are

$$\delta W_{23} = \frac{-\beta_a \Delta_a \cos\phi + \beta_b \Delta_b}{\sin\phi} = \frac{-\beta_a \Delta_a \cos\phi + \beta_b B + \beta_b B' \Delta_a}{\sin\phi}$$

$$= \left(\frac{\beta_b B}{\sin\phi}\right) + \left(\frac{\beta_b B' - \beta_a \cos\phi}{\sin\phi}\right) \Delta_a = P + P' \Delta_a,$$

$$\delta W_{13} = \left(\frac{-\beta_c^* C - P S_2^* M_3^*}{S_1^* M_3^*}\right)$$

$$+ \left(\frac{-\beta_c^* C' + 2\gamma_a S_2^* M_2^* + \beta_a (S_1^* M_2^* + S_2^* M_1^*) - P' S_2^* M_3^*}{S_1^* M_3^*}\right) \Delta_a$$

$$= Q + Q' \Delta_a,$$

$$\delta W_{33} = \left(\frac{\varepsilon_1 + Q \sin 2\phi}{\sin^2\phi}\right) + \left(\gamma_a + \frac{2Q' \cos\phi}{\sin\phi}\right) \Delta_a = R + R' \Delta_a.$$

Finally, putting ε_3 into Equation (7) we obtain

$$\delta\varepsilon_3 = (\varepsilon_2 + 2PM_2^* M_3^* + 2QM_1^* M_3^* + RM_3^{*2}) + [\gamma_a (2S_1^{*2} - 1) - 2\beta_a S_1^* S_2^*$$

$$+ \gamma_a (M_1^{*2} - M_2^{*2}) - 2\beta_a M_1^* M_2^* + 2P' M_2^* M_3^* + 2Q' M_1^* M_3^* + R' M_3^{*2}] \Delta_a$$

$$= -\varepsilon_3,$$

from which the formula for Δ_a given below (Collected Formulas) is obtained.

DISCUSSION

A computer program has been written in Fortran IV for the calculation of g tensors in any of the four cases described. By employing this program with experimental g tensors, the equations of this article were checked. α, β, γ parameters were first obtained from Equations (29) and these were used as input for the computer program. Agreement of the g tensors derived by the program with the original tensors provided a check on the internal consistency of the equations for each of the four cases.

Iterative Solutions

The iterative procedures for the four cases described above may not converge if a starting-angle error is too large (as may happen in using the $\alpha\lambda$ method of Equation (3)), in which case the problem may be solved by setting

$$\Delta_i = \Delta_i(\text{calculated}), \qquad \text{if} |\Delta_i(\text{calcd})| < R_c,$$

$$= R_c \times \text{SIGN}\Delta_i(\text{calcd}), \quad \text{if} |\Delta_i(\text{calcd})| > R_c \quad (i = a,b,c),$$

where SIGNx = $x/|x|$. R_c should be chosen to be within the range of stable convergence which is different for each of the four cases considered below. A safe value for R_c is ~0.2.

From the approximate changes in angles Δ_i one may proceed in two ways:

(i) Calculate exactly the new values of the parameters from

$$\alpha_i' = \alpha_i,$$

$$\beta_i' = \beta_i \cos\Delta_i + \gamma_i \sin\Delta_i,$$

$$\gamma_i' = \gamma_i \cos\Delta_i - \beta_i \sin\Delta_i \quad (i = a,b,c) \tag{33}$$

obtained from Equation (5) and use these again in the equations for the iterative solution to obtain a new set of Δ_i's. This process is continued until either the absolute fractional changes of the α, β, γ parameters are below a certain low value (for the CDC 6500 computer this was set at 1.0×10^{-11}), or until the values of the null functions are negligible. If the approximations for Δ_a, Δ_b, Δ_c, are continually summed, and the final values divided by two, three starting-angle shifts $\delta\theta_a$, $\delta\theta_b$, $\delta\theta_c$ (i.e., the angles <u>from</u> the experimental alignments <u>to</u> the "true" theoretical initial orientations) are obtained.

(ii) Calculate approximately the new values of the parameters from

$$\alpha_i' = \alpha_i, \quad \beta_i' = \beta_i + \gamma_i\Delta_i, \quad \gamma_i' = \gamma_i - \beta_i\Delta_i \quad (i = a,b,c)$$

and continue the process as in the first method. This procedure will converge because the method is self-correcting. The starting angle shifts can then be determined by solving Equations (33), using Appendix A with the initial parameters β_i, γ_i, λ_i and the final parameters β_i', γ_i', to obtain

$$\delta\theta_i = \frac{1}{2}[\cos^{-1}(\beta_i/\lambda_i)\cdot \mathrm{SIGN}\gamma_i \pm \cos^{-1}(\beta_i^t/\lambda_i)] \quad (i = a,b,c).$$

From Equations (8) we can calculate the number of solutions for the starting-angle shifts in each of the four cases. The approximate methods will only give the solution with the smallest starting-angle shifts.

Exact Solutions

The principal values of the g tensor are the square roots of the equation $\overrightarrow{\overrightarrow{W}}\vec{X}_i = E_i\vec{X}_i$ $(i = 1,2,3)$. The principal values E_i solely determine the "shape" of the tensor. The eigenvectors $\vec{X}_i$ determine the orientation of the principal axes and thus the orientation of the tensor. The number of eigenvalue solutions is the number of diagonalized W tensors which are "shaped" differently. The number of eigenvector solutions is the number of diagonalized W tensors which are "shaped" or oriented differently. If we

consider the degeneracy of the solutions to be the number of eigenvector solutions per eigenvalue solution, we find from Equations (8) that the degeneracies of the coplanar, monoclinic, orthorhombic, and general cases to be 2, 2, 4, and 1, respectively. If two of the possible W tensors have the same principal values, and the eigenvectors of one tensor become the eigenvectors of the second tensor when rotated 180° about the axis i, then we call the axis i an axis of degeneracy. The axes of degeneracy account for the degeneracy of the solutions and are listed below.

COLLECTED FORMULAS

The α, β, γ parameters depend on the choice of initial orientations and, to use the formulas of this article, they should be determined with the orientation conventions of Table 1. The W coefficients and null functions for each case are also given in Table 1. The solutions are listed below.

Coplanar Case

Possible number of eigenvalue solutions: 0, 1, 2, 3, 4.

Possible number of eigenvector solutions: 0, 2, 4, 6, 8.

The one axis of degeneracy is the $\vec{c}$ axis (the $\vec{2}$ axis).

The iterative solution is

$$\Delta_a = \frac{\varepsilon_3 + \beta_b B\sin\psi - \beta_c C\sin\phi}{\beta_a \sin(\psi - \phi) - \beta_b B'\sin\psi + \beta_c C'\sin\phi} ,$$

$$\Delta_b = B + B'\Delta_a, \quad B = \varepsilon_1/\gamma_b, \quad B' = \gamma_a/\gamma_b,$$

$$\Delta_c = C + C'\Delta_a, \quad C = \varepsilon_2/\gamma_c, \quad C' = \gamma_a/\gamma c.$$

Table 1. W coefficients and null functions with the necessary "theoretical" initial orientations.

Rotation Axes	Initial Conditions for H when $\theta = 0°$	W Coefficients	Null Functions
		Coplanar Case	
a	H in a b c plane	$W_{11} = \alpha_a + \beta_a \quad W_{22} = \alpha_a - \beta_a \quad W_{12} = \gamma_a$	$\varepsilon_1 = \alpha_b - \beta_b - \alpha_a + \beta_a$
b	H in a b c plane	$W_{23} = (\gamma_a \cos\phi - \gamma_b)/\sin\phi$	$\varepsilon_2 = \alpha_c - \beta_c - \alpha_a + \beta_a$
c	H in a b c plane	$W_{13} = \dfrac{[\beta_a(1 + \cos^2\phi) - 2\beta_b]\sin^2\psi - [\beta_a(1 + \cos^2\psi) - 2\beta_c]\sin^2\phi}{2\sin\phi\sin\psi\sin(\psi - \phi)}$	$\varepsilon_3 = \gamma_a \sin(\psi - \phi) - \gamma_b \sin\psi + \gamma_c \sin\phi$
		$W_{33} = \alpha_a + \dfrac{[\beta_a(1 + \cos^2\phi) - 2\beta_b]\sin 2\psi - [\beta_a(1 + \cos^2\psi) - 2\beta_c]\sin 2\phi}{2\sin\phi\sin\psi\sin(\psi - \phi)}$	
		Monoclinic Case	
a	H in a b plane	$W_{11} = \alpha_a + \beta_a \quad W_{22} = \alpha_a - \beta_a$	$\varepsilon_1 = \alpha_c - \beta_c - \alpha_a - \beta_a$
b	H in a b plane	$W_{12} = \gamma_a \quad W_{13} = \gamma_c \quad W_{33} = \alpha_c + \beta_c$	$\varepsilon_2 = \alpha_c - \beta_c + \alpha_b - \beta_b - 2\alpha_a$
c	H in a c plane	$W_{23} = (\gamma_a \cos\phi - \gamma_b)/\sin\phi$	$\varepsilon_3 = \alpha_b - \alpha_a + \sin\phi(\gamma_c \cos\phi - \beta_c \sin\phi)$
		Orthorhombic Case	
a	H in a b plane	$W_{11} = \alpha_a + \beta_a \quad W_{22} = \alpha_b + \beta_b$	$\varepsilon_1 = \alpha_c - \alpha_b - \beta_a$
b	H in b c plane	$W_{33} = \alpha_c + \beta_c \quad W_{12} = \gamma_a$	$\varepsilon_2 = \alpha_a - \alpha_c - \beta_b$
c	H in c a plane	$W_{23} = \gamma_b \quad W_{13} = \gamma_c$	$\varepsilon_3 = \alpha_b - \alpha_a - \beta_c$
		General Case	
a	H in a b plane	$W_{11} = \alpha_a + \beta_a \quad W_{22} = \alpha_a - \beta_a \quad W_{12} = \gamma_a$	$\varepsilon_1 = \alpha_b - \beta_b - \alpha_a + \beta_a$
b	H in a b plane	$W_{23} = (\gamma_a \cos\phi - \gamma_b)/\sin\phi$	$\varepsilon_2 = \alpha_a + \beta_a(2S_1^{*2} - 1) + 2\gamma_a S_1^* S_2^* - \alpha_c^* - \beta_c^*$
c	H along $\vec{S}^*$ where $S_3^* = 0$ (i.e., in the $\vec{1}\ \vec{2}$ plane)	$W_{13} = [\gamma_c^* + 2\beta_a S_2^* M_2^* - \gamma_a(S_1^* M_2^* + S_2^* M_1^*) - W_{23} S_2^* M_3^*]/S_1^* M_3^*$	$\varepsilon_3 = \alpha_a(1 - M_3^{*2}) + \beta_a(M_1^{*2} - M_2^{*2})$
		$W_{33} = [\alpha_b + \beta_b - (\alpha_a + \beta_a)\cos^2\phi + W_{13}\sin 2\phi]/\sin^2\phi$	$+ 2\gamma_a M_1^* M_2^* + 2W_{23} M_2^* M_3^*$
			$+ 2W_{13} M_1^* M_3^* + W_{33} M_3^{*2} - \alpha_c^* + \beta_c^*$

The exact solution to Equations (7) is complex and thus it is more feasible to use an iterative procedure than the closed form. Some relationships among the various exact solutions of Equations (7) are: If $(\zeta_a, \zeta_b, \zeta_c)$ is a solution, then $(-\zeta_a, -\zeta_b, -\zeta_c)$ is another solution with the properties that (a) its eigenvalues are the same as those of $(\zeta_a, \zeta_b, \zeta_c)$, (b) the signs of W_{12}, W_{23} are changed, and (c) the eigenvectors are rotated 180° about the $\vec{2}$ axis.

Monoclinic Case

Possible number of eigenvalue solutions: 0, 2, 4.

Possible number of eigenvector solutions: 0, 4, 8.

The one axis of degeneracy is the $\vec{c}$ axis (the $\vec{2}$ axis).

The iterative solution is: $\Delta_c = \varepsilon_3/[\sin\phi(\beta_c\cos\phi + \gamma_c\sin\phi)]$,

$$\Delta_b = (\varepsilon_2 - \gamma_c\Delta_c)/\gamma_b, \quad \Delta_a = (\varepsilon_1 - \gamma_c\Delta_c)/\gamma_a.$$

The exact solution is

$$\zeta_c = \begin{cases} \xi_c + \phi \\ \\ \pi - \xi_c + \phi, \end{cases} \quad \zeta_a = \pm\,\xi_a, \quad \zeta_b = \pm\,\xi_b,$$

where

$$\xi_c = \sin^{-1}[(\alpha_a - \alpha_b)/\lambda_c \sin\phi], \quad \xi_a = \cos^{-1}[(\alpha_c - \alpha_a - \lambda_c \cos\zeta_c)/\lambda_a],$$

$$\xi_b = \cos^{-1}[(\alpha_b + \alpha_c - 2\alpha_a - \lambda_c \cos\zeta_c)/\lambda_b].$$

For each of the two choices for ζ_c there are four solutions for ζ_a and ζ_b corresponding to the four choices of sign for these: $(+\xi_a, +\xi_b)$, (--), (+-), (-+), where the first two solutions represent one eigenvalue solution and the last two represent another. Also a rotation of the eigenvectors about the c axis will transform the solutions as follows: (++)→(--), (--)→(++), (+-)→(-+), (-+)→(+-).

The $\alpha\lambda$ solution may be obtained by calculating β_i and γ_i from $\beta_i = \lambda_i \cos\zeta_i$, $\gamma_i = \lambda_i \sin\zeta_i$ (i = a,b,c), using the solutions given above for ζ_a, ζ_b, ζ_c (which depend only on α_i and λ_i). These are then employed in the formulas for the W coefficients.

Orthorhombic Case

Possible number of eigenvalue solutions: 0, 1, 2.

Possible number of eigenvector solutions: 0, 4, 8.

The three axes of degeneracy are the $\vec{a}$, $\vec{b}$, $\vec{c}$ axes (the $\vec{3}$, $\vec{1}$, $\vec{2}$ axes).

The iterative solution is $\Delta_a = \varepsilon_1/\gamma_a$, $\Delta_b = \varepsilon_2/\gamma_b$, $\Delta_c = \varepsilon_3/\gamma_c$.

The exact solution is

$$\zeta_a = \pm \cos^{-1}[(\alpha_c - \alpha_b)/\lambda_a], \quad \zeta_b = \pm \cos^{-1}[(\alpha_a - \alpha_c)/\lambda_b],$$

$$\zeta_c = \pm \cos^{-1}[(\alpha_b - \alpha_a)/\lambda_c].$$

The solutions may be ordered according to the eight possible combinations of signs for the ζ_i: $(+\zeta_a, +\zeta_b, +\zeta_c)$, $(+--)$, $(-+-)$, $(--+)$, $(---)$, $(-++)$, $(+-+)$, $(++-)$. The first four solutions represent one eigenvalue and the last four solutions represent the other. A rotation of 180° about axis a will transform the solutions as follows: $(+++) \rightarrow (+--)$, $(+--) \rightarrow (+++)$, $(---) \rightarrow (-++)$, $(-++) \rightarrow (---)$. Similarly, for a rotation of 180° about axis b: $(+++) \rightarrow (-+-)$, $(-+-) \rightarrow (+++)$, $(---) \rightarrow (+-+)$, $(+-+) \rightarrow (---)$. Finally, for a rotation of 180° about axis c: $(+++) \rightarrow (--+)$, $(--+) \rightarrow (+++)$, $(---) \rightarrow (++-)$, $(++-) \rightarrow (---)$.

The $\alpha\lambda$ solution is

$$W_{11} = \alpha_a - \alpha_b + \alpha_c, \quad W_{22} = \alpha_b - \alpha_c + \alpha_a, \quad W_{33} = \alpha_c - \alpha_a + \alpha_b,$$

$$W_{12} = \pm \sqrt{[\lambda_a^2 - (\alpha_c - \alpha_b)^2]}, \quad W_{23} = \pm \sqrt{[\lambda_b^2 - (\alpha_a - \alpha_c)^2]},$$

$$W_{13} = \pm \sqrt{[\lambda_c^2 - (\alpha_b - \alpha_a)^2]}.$$

General Case

Possible number of eigenvalue solutions: 0, 1, 2, ... 16.

Possible number of eigenvector solutions: 0, 1, 2, ... 16.

There are no axes of degeneracy.

The iterative solution is

$$\Delta_a = \frac{-\varepsilon_3 - \varepsilon_2 - RM_3^{*2} - 2PM_2^*M_3^* - 2QM_1^*M_3^*}{\gamma_a(M_1^{*2} + S_1^{*2} - M_2^{*2} - S_2^{*2}) - 2\beta_a(M_1^*M_2^* + S_1^*S_2^*) + R'M_3^{*2} + 2P'M_2^*M_3^* + 2Q'M_1^*M_3^*}$$

$$\Delta_b = B + B'\Delta_a, \quad \Delta_c = C + C'\Delta_a,$$

where

$$B = \varepsilon_1/\gamma_b, \quad B' = \gamma_a/\gamma_b, \quad C = \varepsilon_2/\gamma_c^*, \quad C' = [\gamma_a(2S_1^{*2} - 1) - 2\beta_a S_1^*S_2^*]/\gamma_c^*.$$

$$P = \beta_b B/\sin\phi, \quad P' = (\beta_b B' - \beta_a\cos\phi)/\sin\phi,$$

$$Q = (-\beta_c^* C - PS_2^*M_3^*)/S_1^*M_3^*,$$

$$Q' = [-\beta_c^* C' + 2\gamma_a S_2^*M_2^* + \beta_a(S_1^*M_2^* + S_2^*M_1^*) - P'S_2^*M_3^*]/S_1^*M_3^*,$$

$$R = (\varepsilon_1 + Q\sin 2\phi)/\sin^2\phi, \quad R' = \gamma_a + (2Q'\cos\phi/\sin\phi).$$

The exact solution is obtained by substituting Equations (6) into Equations (7) which gives the expressions to be solved for ζ_a, ζ_b, ζ_c. Most of the sixteen possible solutions will generally not be acceptable since they will not be real.

PART II

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REFERENCES

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PART II

APPENDICES

APPENDIX A

SOLUTIONS TO A TRIGONOMETRIC EQUATION

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SOLUTIONS TO A TRIGONOMETRIC EQUATION

There are at least four different ways in which the solution to

$$A\cos\theta + B\sin\theta = C \tag{A1}$$

may be written. The most convenient for the present purpose is derived below.

Equation (A1) may be written as $M\cos(\theta - \lambda) = C$, where $M\cos\lambda = A$ and $M\sin\lambda = B$. The relative signs of A and B determine the quadrant of the angle λ. By setting $M = +\sqrt{(A^2 + B^2)}$ it is seen that λ is uniquely determined by

$$\lambda = \cos^{-1}[A/\sqrt{(A^2 + B^2)}] \times \mathrm{SIGN}(B), \tag{A2}$$

where $\mathrm{SIGN}(B) = B/|B|$. Equation (A1) now becomes $\cos\xi = C/\sqrt{(A^2 + B^2)}$, where $\xi = \theta - \lambda$. Since ξ is double valued, the two solutions to Equation (A1) are

$$\theta = \cos^{-1}[A/\sqrt{(A^2 + B^2)}]\cdot\mathrm{SIGN}(B) \pm \cos^{-1}[C/\sqrt{(A^2 + B^2)}]. \tag{A3}$$

APPENDIX B

PROPERTIES OF SECOND-ORDER TENSORS

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PROPERTIES OF SECOND-ORDER TENSORS

If a second-order symmetric tensor $\overline{\overline{W}}$ is diagonalized by the similarity transformation $\overline{\overline{R}}^{-1}\overline{\overline{W}}\overline{\overline{R}}$, then the columns of the unitary matrix $\overline{\overline{R}}$ represent the eigenvectors of the tensor. Changing the signs of any column of $\overline{\overline{R}}$ does not change the eigenvalues (the "shape" of the tensor), or the orientation, of the corresponding diagonalized tensor $\overline{\overline{W}}$. Changing all the signs of the i-th row of $\overline{\overline{R}}$ does not change the eigenvalues but rotates the eigenvectors 180° about axis i, which is the same as reflecting the eigenvectors through the jk plane ($j,k \neq i$). These results are similarly accomplished by changing the signs of four of the off-diagonal elements of the undiagonalized $\overline{\overline{W}}$ tensor: $W_{ij} = W_{ji}$, $W_{ik} = W_{ki}$ ($j \neq k$). This can be shown by considering another matrix $\overline{\overline{R}}^*$ such that $R^*_{pq} = \pm R_{pq}$ [($p,q = 1,3$), ($\pm$) sign if $p(\neq) i$]. Applying this new similarity transformation to $\overline{\overline{W}}$ gives

$$W'^{*}_{lm} = \sum_{jk} (R^{*})^{-1}_{lj} W_{jk} R^{*}_{km} = \sum_{jk} R^{*}_{jl} R^{*}_{km} W_{jk}$$

$$= \sum_{j\neq i} R_{jl} R_{jm} W_{jj} + (-R_{il})(-R_{im}) W_{ii} + \sum_{\substack{j\neq k \\ j,k\neq l}} R_{jl} R_{km} W_{jk}$$

$$+ \sum_{\substack{j\neq k \\ k=i}} (R_{jl})(-R_{im}) W_{ji} + \sum_{\substack{j\neq k \\ j=i}} (-R_{il})(R_{km}) W_{ik},$$

from which we see that if the similarity transform matrix $\overline{\overline{R}}$ diagonalizes $\overline{\overline{W}}$, then $\overline{\overline{R}}^{*}$ diagonalizes the matrix $\overline{\overline{W}}$ with the signs changed on the four off-diagonal elements $W_{ji} = W_{ij}$, $W_{ik} = W_{ki}$.

The eight tensors resulting from the eight possible sign permutations of the off-diagonal elements W_{12}, W_{23}, W_{13} are $(+W_{12}, +W_{23}, +W_{13})$, (-+-), (--+), (+--), (---), (+-+), (++-), (-++). The first four of these have one set of eigenvalues and the last four a second set. A rotation of 180° about axis $\vec{1}$ changes (+++)→(-+-) and (---)→(+-+), about axis $\vec{2}$ changes (+++)→(--+) and (---)→(++-), and about axis $\vec{3}$ changes (+++)→(+--) and (---)→(-++).

APPENDIX C

COMPUTER LISTING OF SUBROUTINES USED FOR THE CALCULATION OF g TENSORS FOR THE COPLANAR, MONOCLINIC, ORTHORHOMBIC, AND GENERAL CASE

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COMPUTER LISTING OF SUBROUTINES USED FOR THE CALCULATION OF G TENSORS FOR THE COPLANAR, MONOCLINIC, ORTHORHOMBIC, AND GENERAL CASE

```
      PROGRAM GTENSOR(INPUT,OUTPUT)                                     GTNSR  1
      REAL NN1,NN2,NN3                                                  GTNSR  2
      COMMON/PARAM/ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                  GTNSR  3
      COMMON/W/W11,W22,W33,W12,W23,W13                                  GTNSR  4
   99 FORMAT(I1)                                                        GTNSR  5
   98 FORMAT(3F10.8)                                                    GTNSR  6
      READ 99,INDEX                                                     GTNSR  7
      READ 98,ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                       GTNSR  8
      GO TO (10,20,30,40) INDEX                                         GTNSR  9
C THIS IS A SAMPLE PROGRAM SHOWING HOW ONE MAY WRITE A PROCEDURE THAT   GTNSR 10
C WOULD CALL ANY OF THE FOUR SUBROUTINES. ONLY THE SUBROUTINE OF        GTNSR 11
C INTEREST NEED BE LOADED INTO THE COMPUTER.                            GTNSR 12
C  ALA,ALB,ALC ARE THE ALPHA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. GTNSR 13
C  BEA,BEB,BEC ARE THE BETA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C.  GTNSR 14
C  GAA,GAB,GAC ARE THE GAMMA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. GTNSR 15
C THESE PARAMETERS ARE TRANSMITTED THROUGH THE LABELLED COMMON /PARAM/. GTNSR 16
C THE W-COEFFICIENTS W11,W22,W33,W12,W23,W13 ARE CALCULATED BY EACH OF  GTNSR 17
C THE SUBROUTINES AND ARE LOCATED IN THE LABELLED COMMON /W/. EACH      GTNSR 18
C SUBROUTINE CALLS DISPLAY AND PASSES THE W-COEFFICIENTS THROUGH /W/.   GTNSR 19
C SUBROUTINE DISPLAY CALLS DIAG1 WHICH IS A STANDARD DIAGONALIZATION    GTNSR 20
C SUBROUTINE. OTHER SUBROUTINES ARE INCLUDED, BUT ARE NEVER CALLED.     GTNSR 21
C THESE SUBROUTINES CAN BE USED TO TEST OR DOUBLE-CHECK THE RESULTS OF  GTNSR 22
C THIS PROGRAM. THE COMMENT CARDS IN EACH SUBROUTINE DESCRIBE THE       GTNSR 23
C QUANTITIES CALCULATED.                                                GTNSR 24
C  ..... COPLANAR CASE .....      (INDEX = 1)                           GTNSR 25
   10 READ 98,PHI,PSI                                                   GTNSR 26
      CALL COPLANR(PHI,PSI)                                             GTNSR 27
      STOP 1111                                                         GTNSR 28
C  ..... MONOCLINIC CASE .....    (INDEX = 2)                           GTNSR 29
   20 READ 98,PHI                                                       GTNSR 30
      CALL MONOCLN(PHI)                                                 GTNSR 31
      STOP 2222                                                         GTNSR 32
C  ..... ORTHORHOMBIC CASE ..... (INDEX = 3)                           GTNSR 33
   30 CALL RHOMBIC                                                      GTNSR 34
      STOP 3333                                                         GTNSR 35
C  ..... GENERAL CASE .....       (INDEX = 4)                           GTNSR 36
   40 READ 98,PHI                                                       GTNSR 37
      READ 98,NN1,NN2,NN3,SS1,SS2,SS3                                   GTNSR 38
      CALL GENERAL(PHI,NN1,NN2,NN3,SS1,SS2,SS3)                         GTNSR 39
      STOP 4444                                                         GTNSR 40
      END                                                               GTNSR 41
      SUBROUTINE COPLANR(PHI,PSI)                                       COPLN  1
C  ..... PHI AND PSI ARE IN DEGREES.                                    COPLN  2
      DIMENSION ANGDEG(3)                                               COPLN  3
      COMMON/PARAM/ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                  COPLN  4
      COMMON/W/W11,W22,W33,W12,W23,W13                                  COPLN  5
      DATA PI/3.14159265359/,TODEG2/28.64788976/,TORAD/0.01745329252/,  COPLN  6
     DNSTEPS/180/,NTRIES/23/                                            COPLN  7
C  ALA,ALB,ALC ARE THE ALPHA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. COPLN  8
C  BEA,BEB,BEC ARE THE BETA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C.  COPLN  9
C  GAA,GAB,GAC ARE THE GAMMA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. COPLN 10
C TODEG2 = 57.29577951/2.0 = (180/PI)/2.  TORAD = PI/180.               COPLN 11
  600 FORMAT(1H1,41X, 23H.... COPLANAR CASE .....,10X,6HPHI = ,1F9.4,3X, COPLN 12
     A6HPSI = ,1F9.4,//,39X,28HTHE ORIGINAL PARAMETERS ARE:, /)         COPLN 13
  601 FORMAT(37X,5HALPHA,11X,4HBETA,12X,5HGAMMA,//,24X,7HAXIS A:,1F16.8,COPLN 14
     B2E16.9//24X,7HAXIS B:,1F16.8,2E16.9//24X,7HAXIS C:,F16.8,2E16.9//)COPLN 15
  602 FORMAT(22X, 38HTHE STARTING-ANGLE ERRORS (IN DEGREES), /, 22X,    COPLN 16
     C29HABOUT THE THREE ROTATION AXES,/,23X,6HAXIS A,6X,6HAXIS B,6X,   COPLN 17
     D6HAXIS C)                                                         COPLN 18
  603 FORMAT(3X,12HSOLUTION NO.,I2,4H... ,F9.4,3X,F9.4,3X,F9.4)         COPLN 19
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  604 FORMAT(/,38X, 48HTHIS SOLUTION HAS THE FOLLOWING ALPHA,BETA,GAMMA,COPLN 20
     E/, 38X,41HPARAMETERS FOR THE THREE AXES OF ROTATION)                COPLN 21
  605 FORMAT(/,27(5H  * ),///,49X,27H... END OF CALCULATIONS ...)          COPLN 22
  700 FORMAT(//, 65H THERE IS AN ERROR. AN ITERATIVE PROCESS DID NOT CONCOPLN 23
     FVERGE WITHIN , I4,11H ITERATIONS,/,36H THE VALUE OF THE NULL FUNCTCOPLN 24
     GIONS ARE,/, 6H E1 = ,E15.9,6H E2 = ,E15.9,6H E3 = ,E15.9,/,         COPLN 25
     H18H ANGA,ANGB,ANGC = , 3E15.9,/)                                    COPLN 26
  701 FORMAT(18H ERROR IN COPLANR0, /, (39X,3E15.9,/))                    COPLN 27
      FE = PHI*TORAD                                                      COPLN 28
      SI = PSI*TORAD                                                      COPLN 29
      SNFE=SIN(FE)                                                        COPLN 30
      SN2FE=SIN(2.0*FE)                                                   COPLN 31
      SNFE2=SNFE**2                                                       COPLN 32
      SNSI=SIN(SI)                                                        COPLN 33
      SN2SI=SIN(2.0*SI)                                                   COPLN 34
      SNSI2=SNSI**2                                                       COPLN 35
      CSSI=COS(SI)                                                        COPLN 36
      CSSI2=CSSI**2                                                       COPLN 37
      CSFE=COS(FE)                                                        COPLN 38
      CSFE2=CSFE**2                                                       COPLN 39
      SNSIFE=SIN(SI-FE)                                                   COPLN 40
      DEN=2.0*SNFE*SNSI*SNSIFE                                            COPLN 41
      ABSTEP = PI/FLOAT(NSTEPS)                                           COPLN 42
      ACCUR = ABSTEP/1000.0                                               COPLN 43
      PRINT 600,PHI,PSI                                                   COPLN 44
      PRINT 601,ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                       COPLN 45
      ZLMDAA=SQRT(BEA**2+GAA**2)                                          COPLN 46
      ZLMDAB=SQRT(BEB**2+GAB**2)                                          COPLN 47
      ZLMDAC=SQRT(BEC**2+GAC**2)                                          COPLN 48
      DPLUSA = SIGN(ACOS(BEA/ZLMDAA),GAA)                                 COPLN 49
      DPLUSB = SIGN(ACOS(BEB/ZLMDAB),GAB)                                 COPLN 50
      DPLUSC = SIGN(ACOS(BEC/ZLMDAC),GAC)                                 COPLN 51
      NSOL=0                                                              COPLN 52
      STEP = SIGN(ABSTEP,DPLUSA)                                          COPLN 53
      X1 = (-ZLMDAB-ALB*ALA)/ZLMDAA                                       COPLN 54
      X2 = (-ZLMDAC-ALC*ALA)/ZLMDAA                                       COPLN 55
      XX1= (+ZLMDAB-ALB*ALA)/ZLMDAA                                       COPLN 56
      XX2= (+ZLMDAC-ALC*ALA)/ZLMDAA                                       COPLN 57
      XLOWER=AMAX1(X1,X2,-1.0)                                            COPLN 58
      XUPPER=AMIN1(XX1,XX2,+1.0)                                          COPLN 59
      IF(XUPPER-XLOWER) 299,299,10                                        COPLN 60
   10 ZTAMAX=ACOS(XLOWER)                                                 COPLN 61
      ZTAMIN=ACOS(XUPPER)                                                 COPLN 62
      IBEG = IFIX(ZTAMIN/ABS(STEP))+1                                     COPLN 63
      IEND = IFIX(ZTAMAX/ABS(STEP))+1                                     COPLN 64
      PNB = +1.0                                                          COPLN 65
      PNC = -1.0                                                          COPLN 66
      DO 201 LMN=1,4                                                      COPLN 67
      T=PNB                                                               COPLN 68
      PNB=-PNC                                                            COPLN 69
      PNC=T                                                               COPLN 70
      KLL=0                                                               COPLN 71
      KSCH=0                                                              COPLN 72
      INDEX=0                                                             COPLN 73
      CROSS=+1.0                                                          COPLN 74
      DO 200 I=IBEG,IEND                                                  COPLN 75
C     ..... INDEX = NUMBER OF STEPS IN ALLOWED REGION.                    COPLN 76
C     ..... KLL = 0 FORBIDDEN REGION                                      COPLN 77
C     ..... KLL = 1 ALLOWED REGION                                        COPLN 78
C     ..... KLLSV = VALUE OF KLL FOR PREVIOUS STEP. ENTERING THE DO LOOP  COPLN 79
C     ..... KSCH = (0,1) IF SEARCH FOR CROSSOVER (DOES NOT,DOES) OCCUR.   COPLN 80
C     ..... KSCHSV = VALUE OF KSCH FOR PREVIOUS STEP.                     COPLN 81
C     FOR THE FIRST TIME CAUSES KLLSV TO BE SET TO 0.                     COPLN 82
C     ..... CROSS IS LESS THAN OR EQUAL TO 0.0 ONLY IF A CROSSOVER IS TO  COPLN 83
C     BE SEARCHED FOR.                                                    COPLN 84
C     ..... FUNC = TEST FUNCTION = E3. WE SEARCH FOR THE ZERO VALUES.     COPLN 85
C     ..... SFUNC = LAST VALUE OF FUNC                                    COPLN 86
C     ..... SSFUNC = SECOND TO THE LAST VALUE OF FUNC                     COPLN 87
      ZTA=FLOAT(I)*STEP                                                   COPLN 88
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      CSZTA=COS(ZTA)                                                    COPLN 89
      KLLSV=KLL                                                         COPLN 90
      KSCHSV=KSCH                                                       COPLN 91
      KSCH=0                                                            COPLN 92
      SSFUNC=SFUNC                                                      COPLN 93
      SFUNC=FUNC                                                        COPLN 94
      CSZTB = (ALB-ALA*ZLMDAA*CSZTA)/ZLMDAB                             COPLN 95
      IF(ABS(CSZTB)-1.0) 38,38,190                                      COPLN 96
   38 CSZTC = (ALC-ALA*ZLMDAA*CSZTA)/ZLMDAC                             COPLN 97
      IF(ABS(CSZTC)-1.0) 39,39,190                                      COPLN 98
C ..... ALLOWED ZONE .....                                              COPLN 99
   39 KLL=1                                                             COPLN100
      INDEX=INDEX+1                                                     COPLN101
C  ..... CALCULATE FUNC ...                                            COPLN102
      SNZTA = SIN(ZTA)                                                  COPLN103
      SNZTB = SIGN((SQRT(1.0-CSZTB**2)),PNB)                            COPLN104
      SNZTC = SIGN((SQRT(1.0-CSZTC**2)),PNC)                            COPLN105
      FUNC = ZLMDAA*SNZTA*SNSIFE-ZLMDAB*SNZTB*SNSI+ZLMDAC*SNZTC*SNFE    COPLN106
C  ..... IF LAST STEP WAS IN THE FORBIDDEN REGION, CHECK FOR CROSSOVER. COPLN107
      IF(KLLSV) 50,100                                                  COPLN108
C  ..... IF INDEX=1, THIS IS THE FIRST STEP AND ANOTHER STEP IS TAKEN.  COPLN109
C  IF FUNC=0.0, THEN THIS WILL BE DETERMINED BY THE PRODUCT SFUNC*FUNC  COPLN110
   50 IF(INDEX-1) 200,200,52                                            COPLN111
   52 CROSS = SFUNC*FUNC                                                COPLN112
C  ..... IF CROSS IS NEGATIVE OR ZERO, A CROSSOVER HAS OCCURED.         COPLN113
      IF(CROSS) 100,100,54                                              COPLN114
C  ..... INDEX MUST BE AT LEAST 3 FOR THE FOLLOWING CHECK TO BE VALID   COPLN115
   54 IF(INDEX-3) 200,56,56                                             COPLN116
C  ..... WE TEST TO SEE IF THE FUNCTION HAS APPROACHED TOWARD AND THEN   COPLN117
C  RETREATED FROM THE FUNC=0.0 AXIS.  THERE ARE TWO CONDITIONS THAT     COPLN118
C  MUST BE MET FOR THIS TO HAVE OCCURED.                                COPLN119
C  (1). (FUNC-SFUNC)*(SFUNC-SSFUNC) MUST BE LESS THAN OR EQUAL TO ZERO  COPLN120
C  (2). FUNC*(FUNC-SFUNC) MUST BE GREATER THAN OR EQUAL TO ZERO.        COPLN121
   56 CHECK = (FUNC-SFUNC)*(SFUNC-SSFUNC)                               COPLN122
      IF(CHECK) 58,58,200                                               COPLN123
   58 CHECK = FUNC*(FUNC-SFUNC)                                         COPLN124
      IF(CHECK) 200,100,100                                             COPLN125
C ..... ROUTINE FOR SEARCHING FOR CROSSOVER POINTS ........             COPLN126
C CALCULATE THE THREE ANGLES ABOUT WHICH THE SEARCH IS TO BEGIN         COPLN127
  100 KSCH=1                                                            COPLN128
C  ..... ANGA,ANGB,ANGC ARE THE (DOUBLE)-STARTING-ANGLE-SHIFTS FOR     COPLN129
C  ROTATIONS ABOUT AXES A,B,C RESPECTIVELY.                             COPLN130
      ANGA = DPLUSA-ZTA                                                 COPLN131
      ANGB = DPLUSB-SIGN(ACOS(CSZTB),PNB)                               COPLN132
      ANGC = DPLUSC-SIGN(ACOS(CSZTC),PNC)                               COPLN133
      JFLAG=0                                                           COPLN134
      GO TO 112                                                         COPLN135
  110 ANGA=ANGA+DELA                                                    COPLN136
      ANGB=ANGB+DELB                                                    COPLN137
      ANGC=ANGC+DELC                                                    COPLN138
  112 CSA=COS(ANGA)                                                     COPLN139
      CSB=COS(ANGB)                                                     COPLN140
      CSC=COS(ANGC)                                                     COPLN141
      SNA=SIN(ANGA)                                                     COPLN142
      SNB=SIN(ANGB)                                                     COPLN143
      SNC=SIN(ANGC)                                                     COPLN144
      BEAK=BEA*CSA+GAA*SNA                                              COPLN145
      BEBK=BEB*CSB+GAB*SNB                                              COPLN146
      BECK=BEC*CSC+GAC*SNC                                              COPLN147
      GAAK=GAA*CSA-BEA*SNA                                              COPLN148
      GABK=GAB*CSB-BEB*SNB                                              COPLN149
      GACK=GAC*CSC-BEC*SNC                                              COPLN150
      E1 = ALB-BEBK-ALA*BEAK                                            COPLN151
      E2 = ALC-BECK-ALA*BEAK                                            COPLN152
      E3 = GAAK*SNSIFE-GABK*SNSI+GACK*SNFE                              COPLN153
      B = E1/GABK                                                       COPLN154
      BP = GAAK/GABK                                                    COPLN155
      C = E2/GACK                                                       COPLN156
      CP = GAAK/GACK                                                    COPLN157
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      F1 = E3*BEBK*B*SNSI-BECK*C*SNFE                                   COPLN158
      F2 = BEAK*SNSIFE-BEBK*BP*SNSI+BECK*CP*SNFE                        COPLN159
      DELA=F1/F2                                                        COPLN160
      DELB=B+BP*DELA                                                    COPLN161
      DELC=C+CP*DELA                                                    COPLN162
      XXA = ABS(DELA)                                                   COPLN163
      IF(JFLAG) 299,114,119                                             COPLN164
  114 IF(XXA-ABSTEP) 119,119,115                                        COPLN165
  115 IF(CROSS) 119,119,200                                             COPLN166
  119 JFLAG = JFLAG+1                                                   COPLN167
      IF(JFLAG-NTRIES) 120,120,195                                      COPLN168
  120 XXB = ABS(DELB)                                                   COPLN169
      XXC = ABS(DELC)                                                   COPLN170
      XX = AMAX1(XXA,XXB,XXC)                                           COPLN171
      IF(XX-ACCUR) 130,130,123                                          COPLN172
  123 IF(XXA-ABSTEP) 125,125,124                                        COPLN173
  124 DELA = SIGN(ABSTEP,DELA)                                          COPLN174
  125 IF(XXB-ABSTEP) 127,127,126                                        COPLN175
  126 DELB = SIGN(ABSTEP,DELB)                                          COPLN176
  127 IF(XXC-ABSTEP) 110,110,128                                        COPLN177
  128 DELC = SIGN(ABSTEP,DELC)                                          COPLN178
  130 DO 180 KABC=1,2                                                   COPLN179
C  ..... FIRST TIME THROUGH THE DO LOOP ANGA=ANGA,ETC. AND GAAK=GAAK,ETCCOPLN180
C  ..... NEXT TIME, ANGA = 2*DPLUSA-ANGA,ETC. AND GAAK=-GAAK,ETC.      COPLN181
      ANGA = FLOAT(2-KABC)*ANGA+FLOAT(KABC-1)*(2.0*DPLUSA-ANGA)         COPLN182
      ANGB = FLOAT(2-KABC)*ANGB+FLOAT(KABC-1)*(2.0*DPLUSB-ANGB)         COPLN183
      ANGC = FLOAT(2-KABC)*ANGC+FLOAT(KABC-1)*(2.0*DPLUSC-ANGC)         COPLN184
      GAAK = FLOAT(3-2*KABC)*GAAK                                       COPLN185
      GABK = FLOAT(3-2*KABC)*GABK                                       COPLN186
      GACK = FLOAT(3-2*KABC)*GACK                                       COPLN187
      ANGDEG(1) = ANGA*TODEG2                                           COPLN188
      ANGDEG(2) = ANGB*TODEG2                                           COPLN189
      ANGDEG(3) = ANGC*TODEG2                                           COPLN190
C CHANGE THE STARTING-ANGLE SHIFT SO THAT ITS MAGNITUDE IS LESS THAN 90 COPLN191
C DEGREES. TO ADD OR SUBTRACT 180 DEGREES DOES NOT AFFECT THE SOLUTION. COPLN192
      DO 140 K=1,3                                                      COPLN193
  136 XZ = ABS(ANGDEG(K))-90.0                                          COPLN194
      IF(XZ) 140,140,137                                                COPLN195
  137 ANGDEG(K) = ANGDEG(K)-SIGN(180.0,ANGDEG(K))                       COPLN196
      GO TO 136                                                         COPLN197
  140 CONTINUE                                                          COPLN198
      NSOL=NSOL+1                                                       COPLN199
      PRINT 602                                                         COPLN200
      PRINT 603,NSOL,ANGDEG                                             COPLN201
      PRINT 604                                                         COPLN202
      PRINT 601,ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                     COPLN203
      W11 = ALA*BEAK                                                    COPLN204
      W22 = ALA-BEAK                                                    COPLN205
      W12 = GAAK                                                        COPLN206
      W23 = (GAAK*CSFE-GABK)/SNFE                                       COPLN207
          Q1 = BEAK*(1.0+CSFE2)-2.0*BEBK                                COPLN208
          Q2 = BEAK*(1.0+CSSI2)-2.0*BECK                                COPLN209
      W33 = ALA+(Q1*SN2SI-Q2*SN2FE)/DEN                                 COPLN210
      W13 =      (Q1*SNSI2-Q2*SNFE2)/DEN                                COPLN211
      CALL DISPLAY(1)                                                   COPLN212
  180 CONTINUE                                                          COPLN213
      GO TO 200                                                         COPLN214
C  ..... FORBIDDEN ZONE ... IF LAST STEP WAS IN ALLOWED ZONE AND A      COPLN215
C  CROSSOVER SEARCH WAS NOT PERFORMED, THEN CHECK FOR CROSSOVER POINT    COPLN216
C  AFTER RESETTING THE PREVIOUS VALUES OF ZTA,CSZTA,CSZTB,CSZTC.         COPLN217
  190 INDEX=0                                                           COPLN218
      KLL=0                                                             COPLN219
      IF(KLLSV) 192,200                                                 COPLN220
  192 IF(KSCHSV) 200,193                                                COPLN221
  193 ZTA=ZTA-STEP                                                      COPLN222
      CSZTA=COS(ZTA)                                                    COPLN223
      CSZTB = (ALB-ALA*ZLMDAA*CSZTA)/ZLMDAB                             COPLN224
      CSZTC = (ALC-ALA*ZLMDAA*CSZTA)/ZLMDAC                             COPLN225
      GO TO 100                                                         COPLN226
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C ..... NO CROSSOVER HAS BEEN FOUND. IF CROSS IS LESS THAN 0.0, ERROR  COPLN227
  195 IF(CROSS) 197,197,200                                            COPLN228
  197 CROSS=+1.0                                                       COPLN229
      PRINT 700,NTRIES,E1,E2,E3,ANGA,ANGB,ANGC                         COPLN230
  200 CONTINUE                                                         COPLN231
  201 CONTINUE                                                         COPLN232
      PRINT 605                                                        COPLN233
      RETURN                                                           COPLN234
  299 PRINT 701,ZLMDAA,ZLMDAB,ZLMDAC,ALA,ALB,ALC,X1,X2,XX1,XX2,XLOWER, COPLN235
     XXUPPER                                                           COPLN236
      RETURN                                                           COPLN237
      END                                                              COPLN238
      SUBROUTINE MONOCLN(PHI)                                          MONOC  1
C ..... PHI IS IN DEGREES.                                             MONOC  2
      DIMENSION ANGDEG(3)                                              MONOC  3
      COMMON/PARAM/ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                 MONOC  4
      COMMON/W/W11,W22,W33,W12,W23,W13                                 MONOC  5
      DATA PI/3.14159265359/,TODEG2/28.64788976/,TORAD/0.01745329252/, MONOC  6
     ONTRIES/23/                                                       MONOC  7
C  ALA,ALB,ALC ARE THE ALPHA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. MONOC  8
C  BEA,BEB,BEC ARE THE BETA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C.  MONOC  9
C  GAA,GAB,GAC ARE THE GAMMA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. MONOC 10
C TODEG2 = 57.29577951/2.0 = (180/PI)/2.  TORAD = PI/180.              MONOC 11
  600 FORMAT(1H1, 37X,25H.... MONOCLINIC CASE .....,10X,6HPHI = ,1F9.4, MONOC 12
     A//,39X,28HTHE ORIGINAL PARAMETERS ARE:, /)                       MONOC 13
  601 FORMAT(37X,5HALPHA,11X,4HBETA,12X,5HGAMMA,//,24X,7HAXIS A:,1F16.8,MONOC 14
     B2E16.9//24X,7HAXIS B:,1F16.8,2E16.9//24X,7HAXIS C:,F16.8,2E16.9//)MONOC 15
  602 FORMAT(22X, 38HTHE STARTING-ANGLE ERRORS (IN DEGREES), /, 22X,     MONOC 16
     C29HABOUT THE THREE ROTATION AXES,/,23X,6HAXIS A,6X,6HAXIS B,6X,   MONOC 17
     D6HAXIS C)                                                        MONOC 18
  603 FORMAT(3X,12HSOLUTION NO.. I2,4H... ,F9.4,3X,F9.4,3X,F9.4)       MONOC 19
  604 FORMAT(/,38X, 48HTHIS SOLUTION HAS THE FOLLOWING ALPHA,BETA,GAMMA,MONOC 20
     E/, 38X,41HPARAMETERS FOR THE THREE AXES OF ROTATION)             MONOC 21
  605 FORMAT(/,27(5H  *  ),///,49X,27H... END OF CALCULATIONS ...)      MONOC 22
  700 FORMAT(//, 65H THERE IS AN ERROR. AN ITERATIVE PROCESS DID NOT CONMONOC 23
     FVERGE WITHIN , I4,11H ITERATIONS,/,36H THE VALUE OF THE NULL FUNCTMONOC 24
     GIONS ARE,/, 6H E1 = ,E15.9,6H E2 = ,E15.9,6H E3 = ,E15.9,/,      MONOC 25
     H18H ANGA,ANGB,ANGC = , 3E15.9,/)                                 MONOC 26
 1999 FORMAT(17H ERROR IN MONOCLN,/, (9X,6E15.9,/))                    MONOC 27
      FE = PHI*TORAD                                                   MONOC 28
      PRINT 600,PHI                                                    MONOC 29
      PRINT 601,ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                    MONOC 30
      NSOL = 0                                                         MONOC 31
      SNFE = SIN(FE)                                                   MONOC 32
      CSFE = COS(FE)                                                   MONOC 33
      ACCUR = PI/18000.0                                               MONOC 34
      NTRIES=30                                                        MONOC 35
      ZLMDAA=SQRT(BEA**2+GAA**2)                                       MONOC 36
      ZLMDAB=SQRT(BEB**2+GAB**2)                                       MONOC 37
      ZLMDAC=SQRT(BEC**2+GAC**2)                                       MONOC 38
      DPLUSA = SIGN(ACOS(BEA/ZLMDAA),GAA)                              MONOC 39
      DPLUSB = SIGN(ACOS(BEB/ZLMDAB),GAB)                              MONOC 40
      DPLUSC = SIGN(ACOS(BEC/ZLMDAC),GAC)                              MONOC 41
      SNCHIC = (ALA-ALB)/(ZLMDAC*SNFE)                                 MONOC 42
      IF(ABS(SNCHIC)-1.0) 8,8,999                                      MONOC 43
    8 CHIC = ASIN(SNCHIC)                                              MONOC 44
      DO 80 KK=1,2                                                     MONOC 45
      ZETAC = FLOAT(2-KK)*(CHIC+FE)+FLOAT(KK-1)*(PI-CHIC+FE)           MONOC 46
      CSZTAC = COS(ZETAC)                                              MONOC 47
      CSCHIB = (ALB+ALC-2.0*ALA-ZLMDAC*CSZTAC)/ZLMDAB                  MONOC 48
      IF(ABS(CSCHIB)-1.0) 10,10,999                                    MONOC 49
   10 CHIB = ACOS(CSCHIB)                                              MONOC 50
      CSCHIA = (ALC-ALA-ZLMDAC*CSZTAC)/ZLMDAA                          MONOC 51
      IF(ABS(CSCHIA)-1.0) 12,12,999                                    MONOC 52
   12 CHIA = ACOS(CSCHIA)                                              MONOC 53
      DO 80 LL=1,2                                                     MONOC 54
      ZETAA = CHIA                                                     MONOC 55
      ZETAB = FLOAT(3-2*LL)*CHIB                                       MONOC 56
C  ..... ANGA,ANGB,ANGC ARE THE (DOUBLE)-STARTING-ANGLE-SHIFTS FOR     MONOC 57
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C  ROTATIONS ABOUT AXES A,B,C RESPECTIVELY.                                    MONOC 58
      ANGA = DPLUSA-ZETAA                                                     MONOC 59
      ANGB = DPLUSB-ZETAB                                                     MONOC 60
      ANGC = DPLUSC-ZETAC                                                     MONOC 61
      JFLAG=0                                                                 MONOC 62
      GO TO 17                                                                MONOC 63
   15 ANGA = ANGA+DELA                                                        MONOC 64
      ANGB = ANGB+DELB                                                        MONOC 65
      ANGC = ANGC+DELC                                                        MONOC 66
   17 CSA = COS(ANGA)                                                         MONOC 67
      CSB = COS(ANGB)                                                         MONOC 68
      CSC = COS(ANGC)                                                         MONOC 69
      SNA = SIN(ANGA)                                                         MONOC 70
      SNB = SIN(ANGB)                                                         MONOC 71
      SNC = SIN(ANGC)                                                         MONOC 72
      BEAK=BEA*CSA+GAA*SNA                                                    MONOC 73
      BEBK=BEB*CSB+GAB*SNB                                                    MONOC 74
      BECK=BEC*CSC+GAC*SNC                                                    MONOC 75
      GAAK=GAA*CSA-BEA*SNA                                                    MONOC 76
      GABK=GAB*CSB-BEB*SNB                                                    MONOC 77
      GACK=GAC*CSC-BEC*SNC                                                    MONOC 78
      E1 = ALC-BECK-ALA-BEAK                                                  MONOC 79
      E2 = ALC-BECK+ALB-BEBK-2.0*ALA                                          MONOC 80
      E3 = ALB-ALA+SNFE*(GACK*CSFE-BECK*SNFE)                                 MONOC 81
      DELC = E3/(SNFE*(BECK*CSFE+GACK*SNFE))                                  MONOC 82
      DELB = (E2-GACK*DELC)/GABK                                              MONOC 83
      DELA = (E1-GACK*DELC)/GAAK                                              MONOC 84
      JFLAG=JFLAG+1                                                           MONOC 85
      IF(JFLAG-NTRIES) 20,19,19                                               MONOC 86
   19 PRINT 700,NTRIES,E1,E2,E3,ANGA,ANGB,ANGC                                MONOC 87
      GO TO 25                                                                MONOC 88
   20 XXA = ABS(DELA)                                                         MONOC 89
      XXB = ABS(DELB)                                                         MONOC 90
      XXC = ABS(DELC)                                                         MONOC 91
      XX = AMAX1(XXA,XXB,XXC)                                                 MONOC 92
      IF(XX-ACCUR) 25,25,15                                                   MONOC 93
   25 DO 80 MM=1,2                                                            MONOC 94
C  ..... FIRST TIME THROUGH THE DO LOOP ANGB=ANGB,ETC. AND GABK=GABK,ETC     MONOC 95
C  ..... NEXT TIME, ANGB = 2*DPLUSB-ANGB,ETC. AND GABK=-GABK,ETC.            MONOC 96
      ANGB = FLOAT(2-MM)*ANGB+FLOAT(MM-1)*(2.0*DPLUSB-ANGB)                   MONOC 97
      ANGA = FLOAT(2-MM)*ANGA+FLOAT(MM-1)*(2.0*DPLUSA-ANGA)                   MONOC 98
      GABK = FLOAT(3-2*MM)*GABK                                               MONOC 99
      GAAK = FLOAT(3-2*MM)*GAAK                                               MONOC100
      ANGDEG(1) = ANGA*TODEG2                                                 MONOC101
      ANGDEG(2) = ANGB*TODEG2                                                 MONOC102
      ANGDEG(3) = ANGC*TODEG2                                                 MONOC103
C CHANGE THE STARTING-ANGLE SHIFT SO THAT ITS MAGNITUDE IS LESS THAN 90       MONOC104
C DEGREES. TO ADD OR SUBTRACT 180 DEGREES DOES NOT AFFECT THE SOLUTION.       MONOC105
      DO 50 K=1,3                                                             MONOC106
   46 XZ = ABS(ANGDEG(K))-90.0                                                MONOC107
      IF(XZ) 50,50,47                                                         MONOC108
   47 ANGDEG(K) = ANGDEG(K)-SIGN(180.0,ANGDEG(K))                             MONOC109
      GO TO 46                                                                MONOC110
   50 CONTINUE                                                                MONOC111
      NSOL=NSOL+1                                                             MONOC112
      PRINT 602                                                               MONOC113
      PRINT 603,NSOL,ANGDEG                                                   MONOC114
      PRINT 604                                                               MONOC115
      PRINT 601,ALA,BEAK,GAAK,ALB,BEBK,GABK,ALC,BECK,GACK                     MONOC116
      W11 = ALA+BEAK                                                          MONOC117
      W22 = ALA-BEAK                                                          MONOC118
      W33 = ALC+BECK                                                          MONOC119
      W12 = GAAK                                                              MONOC120
      W13 = GACK                                                              MONOC121
      W23 = (GAAK*CSFE-GABK)/SNFE                                             MONOC122
      CALL DISPLAY(2)                                                         MONOC123
   80 CONTINUE                                                                MONOC124
      PRINT 605                                                               MONOC125
      RETURN                                                                  MONOC126
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  999 PRINT 1999,ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC,BEAK,GAAK,BEBK,GABKMONOC127
     K,BECK,GACK,E1,E2,E3,DELA,DELB,DELC,ANGA,ANGB,ANGC,DPLUSA,DPLUSB,  MONOC128
     BDPLUSC,ZETAA,ZETAB,ZETAC,ACCUR                                    MONOC129
      RETURN                                                            MONOC130
      END                                                               MONOC131
      SUBROUTINE RHOMBIC                                                RHOMB  1
      DIMENSION ANGLES(3,8),LL(3),LSIGN(3,8),LS0(3,3,8),NSOL(8)         RHOMB  2
      COMMON/PARAM/ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                  RHOMB  3
      COMMON/W/W11,W22,W33,W12,W23,W13                                  RHOMB  4
      DATA PI/3.14159265359/,TODEG2/28.64788976/,NTRIES/30/,KHA/1HA/,   RHOMB  5
     DKHB/1HB/,KHC/1HC/,IY1/1/,IY2/2/,IY3/3/,IY4/4/,IY5/5/,IY6/6/,      RHOMB  6
     DIY7/7/,IY8/8/                                                     RHOMB  7
C  ALA,ALB,ALC ARE THE ALPHA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. RHOMB  8
C  BEA,BEB,BEC ARE THE BETA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C.  RHOMB  9
C  GAA,GAB,GAC ARE THE GAMMA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. RHOMB 10
C TODEG2 = 57.29577951/2.0 = (180/PI)/2.                               RHOMB 11
  600 FORMAT(1H1, 37X,27H.... ORTHORHOMBIC CASE ....., //,39X, 28HTHE ORIRHOMB 12
     AGINAL PARAMETERS ARE:,/)                                          RHOMB 13
  601 FORMAT(37X,5HALPHA,11X,4HBETA,12X,5HGAMMA,//,24X,7HAXIS A:,1F16.8,RHOMB 14
     B2E16.9//24X,7HAXIS B:,1F16.8,2E16.9//24X,7HAXIS C:,F16.8,2E16.9//)RHOMB 15
  602 FORMAT(22X, 38HTHE STARTING-ANGLE ERRORS (IN DEGREES), /, 22X,    RHOMB 16
     C29HABOUT THE THREE ROTATION AXES,/,23X,6HAXIS A,6X,6HAXIS B,6X,   RHOMB 17
     D6HAXIS C)                                                         RHOMB 18
  603 FORMAT(3X,12HSOLUTION NO., I2,4H... ,F9.4,3X,F9.4,3X,F9.4)        RHOMB 19
  604 FORMAT(/, 27X,62HTHESE 8 SOLUTIONS HAVE THE SAME ALPHA AND BETA PARHOMB 20
     ERAMETERS. THE,  /, 27X,62HSIGNS OF THE GAMMA PARAMETERS ARE DIFFERRHOMB 21
     FENT FOR EACH SOLUTION.,/, 85X, 8(6HSOLTN ),/,38X,5HALPHA,10X,     RHOMB 22
     G4HBETA,15X,5HGAMMA,7X,8(4H NO.,I2),/, (21X,5HAXIS ,1A1,1H:,F16.8, RHOMB 23
     H4X,E15.9,5H (+-),E14.9,3X, 8(2H (,1A1,3H)  ),/))                  RHOMB 24
  605 FORMAT(/, 17X,16HTHE W TENSOR IS:, 2X,3(E15.9,2X),//35X,3(E15.9,  RHOMB 25
     I2X),//35X,3(E15.9,2X),/)                                          RHOMB 26
  606 FORMAT( 7X,129HTHE SIGNS TO BE ASSOCIATED WITH THE ELEMENTS OF THERHOMB 27
     J W-TENSOR GIVEN ABOVE ARE ARRANGED IN A CORRESPONDING MATRIX FOR ERHOMB 28
     KACH SOLUTION, //, 2X, 8(5X,9HSOLTN NO.,I2),/, 3(9X, 8(3X,1A1,1X,  RHOMB 29
     L1A1,1X,1A1,,8X), /))                                              RHOMB 30
  607 FORMAT( 2X,26HTHE RESULTS FOR SOLUTIONS ,I1,1H,I1,1H,I1,1H,I1,    RHOMB 31
     M16H ARE GIVEN BELOW,/, 27(5H  *  ))                               RHOMB 32
  608 FORMAT( /, 19X,41HABOVE ARE THE RESULTS FOR SOLUTION NUMBER,I2,   RHOMB 33
     N1H.,/, 19X,82HTO OBTAIN THE OTHER SOLUTIONS, CHANGE THE SIGNS OF ORHOMB 34
     ONE COLUMN OF DIRECTION COSINES,/, 19X,73HAND CHANGE THE CORRESPONDRHOMB 35
     PING COLUMN OF ANGLES BY SUBTRACTING 180 DEGREES., //, (19X,19HFOR RHOMB 36
     @SOLUTION NUMBER, I2, 29H CHANGE THE COLUMN UNDER AXIS, I2,/))     RHOMB 37
  609 FORMAT(27(5H  *  ),/)                                             RHOMB 38
  610 FORMAT(49X,27H... END OF CALCULATIONS ...)                        RHOMB 39
  611 FORMAT(//,34X,24H... ERROR IN RHOMBIC: XZ,1A1,11H = COS(ZETA,1A1, RHOMB 40
     R4H) = ,1F10.6)                                                    RHOMB 41
  612 FORMAT(55X,20HHAS BEEN CHANGED TO ,1F10.6,/)                      RHOMB 42
  700 FORMAT(//, 65H THERE IS AN ERROR. AN ITERATIVE PROCESS DID NOT CONRHOMB 43
     SVERGE WITHIN , I4,11H ITERATIONS,/,36H THE VALUE OF THE NULL FUNCTRHOMB 44
     TIONS ARE,/, 6H E1 = ,E15.9,6H E2 = ,E15.9,6H E3 = ,E15.9,/,       RHOMB 45
     U18H ANGA,ANGB,ANGC = , 3E15.9,/)                                  RHOMB 46
      PRINT 600                                                         RHOMB 47
      PRINT 601,ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                    RHOMB 48
      ACCUR = PI/18000.0                                                RHOMB 49
      ZLMDAA=SQRT(BEA**2+GAA**2)                                        RHOMB 50
      ZLMDAB=SQRT(BEB**2+GAB**2)                                        RHOMB 51
      ZLMDAC=SQRT(BEC**2+GAC**2)                                        RHOMB 52
      DPLUSA = SIGN(ACOS(BEA/ZLMDAA),GAA)                               RHOMB 53
      DPLUSB = SIGN(ACOS(BEB/ZLMDAB),GAB)                               RHOMB 54
      DPLUSC = SIGN(ACOS(BEC/ZLMDAC),GAC)                               RHOMB 55
      XZA=(ALC-ALB)/ZLMDAA                                              RHOMB 56
      XZB=(ALA-ALC)/ZLMDAB                                              RHOMB 57
      XZC=(ALB-ALA)/ZLMDAC                                              RHOMB 58
      KERROR = 0                                                        RHOMB 59
C KERROR = (0,1) IF EITHER XZA,XZB,OR XZC (HAS NOT,HAS) BEEN CHANGED TO RHOMB 60
C TO ALLOW A SOLUTION TO EXIST.                                         RHOMB 61
      YY = ABS(XZA)                                                     RHOMB 62
      IF(YY-1.0) 4,4,2                                                  RHOMB 63
    2 KERROR = 1                                                        RHOMB 64
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      PRINT 611,KHA,KHA,XZA                                          RHOMB 65
      XZA = SIGN(1.0,XZA)                                            RHOMB 66
      PRINT 612,XZA                                                  RHOMB 67
    4 YY = ABS(XZB)                                                  RHOMB 68
      IF(YY-1.0) 8,8,6                                               RHOMB 69
    6 KERROR = 1                                                     RHOMB 70
      PRINT 611,KHB,KHB,XZB                                          RHOMB 71
      XZB = SIGN(1.0,XZB)                                            RHOMB 72
      PRINT 612,XZB                                                  RHOMB 73
    8 YY = ABS(XZC)                                                  RHOMB 74
      IF(YY-1.0) 12,12,10                                            RHOMB 75
   10 KERROR = 1                                                     RHOMB 76
      PRINT 611,KHC,KHC,XZC                                          RHOMB 77
      XZC = SIGN(1.0,XZC)                                            RHOMB 78
      PRINT 612,XZC                                                  RHOMB 79
   12 ZETAA = ACOS(XZA)                                              RHOMB 80
      ZETAB = ACOS(XZB)                                              RHOMB 81
      ZETAC = ACOS(XZC)                                              RHOMB 82
      PM = -1.0                                                      RHOMB 83
      DO 25 II=1,2                                                   RHOMB 84
      PM=-PM                                                         RHOMB 85
C  ..... ANGA,ANGB,ANGC ARE THE (DOUBLE)-STARTING-ANGLE-SHIFTS FOR   RHOMB 86
C  ROTATIONS ABOUT AXES A,B,C RESPECTIVELY.                          RHOMB 87
      ANGA =  DPLUSA-SIGN(ZETAA,PM)                                  RHOMB 88
      ANGB =  DPLUSB-SIGN(ZETAB,PM)                                  RHOMB 89
      ANGC =  DPLUSC-SIGN(ZETAC,PM)                                  RHOMB 90
      JFLAG=0                                                        RHOMB 91
   15 CSA=COS(ANGA)                                                  RHOMB 92
      CSB=COS(ANGB)                                                  RHOMB 93
      CSC=COS(ANGC)                                                  RHOMB 94
      SNA=SIN(ANGA)                                                  RHOMB 95
      SNB=SIN(ANGB)                                                  RHOMB 96
      SNC=SIN(ANGC)                                                  RHOMB 97
      BEAK=BEA*CSA+GAA*SNA                                           RHOMB 98
      BEBK=BEB*CSB+GAB*SNB                                           RHOMB 99
      BECK=BEC*CSC+GAC*SNC                                           RHOMB100
      GAAK=GAA*CSA-BEA*SNA                                           RHOMB101
      GABK=GAB*CSB-BEB*SNB                                           RHOMB102
      GACK=GAC*CSC-BEC*SNC                                           RHOMB103
      E1 = ALC-ALB-BEAK                                              RHOMB104
      E2 = ALA-ALC-BEBK                                              RHOMB105
      E3 = ALB-ALA-BECK                                              RHOMB106
      DELA = E1/GAAK                                                 RHOMB107
      DELB = E2/GABK                                                 RHOMB108
      DELC = E3/GACK                                                 RHOMB109
C IF KERROR = 1, THEN WE CAN NOT FIND A SELF-CONSISTENT SOLUTION, SO WE RHOMB110
C ALLOW THIS APPROXIMATION TO BYPASS THE CHECKING OF DELA,DELB,DELC.   RHOMB111
      IF(KERROR) 21,17,21                                            RHOMB112
   17 ANGA=ANGA+DELA                                                 RHOMB113
      ANGB=ANGB+DELB                                                 RHOMB114
      ANGC=ANGC+DELC                                                 RHOMB115
      JFLAG=JFLAG+1                                                  RHOMB116
      IF(JFLAG-NTRIES) 19,19,18                                      RHOMB117
   18 PRINT 700,NTRIES,E1,E2,E3,ANGA,ANGB,ANGC                       RHOMB118
      GO TO 21                                                       RHOMB119
   19 XXA = ABS(DELA)                                                RHOMB120
      XXB = ABS(DELB)                                                RHOMB121
      XXC = ABS(DELC)                                                RHOMB122
      XX = AMAX1(XXA,XXB,XXC)                                        RHOMB123
      IF(XX-ACCUR) 21,15,15                                          RHOMB124
   21 IJ=4*II-3                                                      RHOMB125
      ANGLES(1,IJ)=ANGA                                              RHOMB126
      ANGLES(2,IJ)=ANGB                                              RHOMB127
      ANGLES(3,IJ)=ANGC                                              RHOMB128
   25 CONTINUE                                                       RHOMB129
      XA=(ANGLES(1,5)-ANGLES(1,1))/2.0                               RHOMB130
      XB=(ANGLES(2,5)-ANGLES(2,1))/2.0                               RHOMB131
      XC=(ANGLES(3,5)-ANGLES(3,1))/2.0                               RHOMB132
      BEAK=ZLMDAA*COS(XA)                                            RHOMB133
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      GAAK=ZLMDAA*SIN(XA)                                                RHOMB134
      BEBK=ZLMDAB*COS(XB)                                                RHOMB135
      GABK=ZLMDAB*SIN(XB)                                                RHOMB136
      BECK=ZLMDAC*COS(XC)                                                RHOMB137
      GACK=ZLMDAC*SIN(XC)                                                RHOMB138
      GAAB = ABS(GAAK)                                                   RHOMB139
      GABB = ABS(GABK)                                                   RHOMB140
      GACB = ABS(GACK)                                                   RHOMB141
C CHANGE THE STARTING-ANGLE SHIFT SO THAT ITS MAGNITUDE IS LESS THAN 90  RHOMB142
C DEGREES. TO ADD OR SUBTRACT 180 DEGREES DOES NOT AFFECT THE SOLUTION.  RHOMB143
      DO 30 K=1,5,4                                                      RHOMB144
      DO 30 J=1,3                                                        RHOMB145
      XX = ANGLES(J,K)*TODEG2                                            RHOMB146
   27 XZ = ABS(XX)-90.0                                                  RHOMB147
      IF(XZ) 30,30,28                                                    RHOMB148
   28 XX = XX-SIGN(180.0,XX)                                             RHOMB149
      GO TO 27                                                           RHOMB150
   30 ANGLES(J,K) = XX                                                   RHOMB151
      DO 32 I=1,3                                                        RHOMB152
      LSIGN(I,1) = 1H+                                                   RHOMB153
   32 LSIGN(I,5) = 1H+                                                   RHOMB154
      IF(GAAK) 33,34,34                                                  RHOMB155
   33 LSIGN(1,1) = 1H-                                                   RHOMB156
   34 IF(GABK) 35,36,36                                                  RHOMB157
   35 LSIGN(2,1) = 1H-                                                   RHOMB158
   36 IF(GACK) 37,38,38                                                  RHOMB159
   37 LSIGN(3,1) = 1H-                                                   RHOMB160
   38 DO 40 I=1,3                                                        RHOMB161
      MM = LSIGN(I,1)-1H+                                                RHOMB162
      IF(MM) 40,39,40                                                    RHOMB163
   39 LSIGN(I,5) = 1H-                                                   RHOMB164
   40 CONTINUE                                                           RHOMB165
      LL(1)=+2                                                           RHOMB166
      LL(2)=-2                                                           RHOMB167
      LL(3)=+2                                                           RHOMB168
      DO 45 IB=2,4                                                       RHOMB169
      DO 42 IA=1,3                                                       RHOMB170
      ANGLES(IA,IB)   = ANGLES(IA,3+LL(IA))                              RHOMB171
      ANGLES(IA,IB+4) = ANGLES(IA,3-LL(IA))                              RHOMB172
      LSIGN(IA,IB)    = LSIGN(IA,3+LL(IA))                               RHOMB173
   42 LSIGN(IA,IB+4) = LSIGN(IA,3-LL(IA))                                RHOMB174
      IT=LL(3)                                                           RHOMB175
      LL(3)=LL(2)                                                        RHOMB176
      LL(2)=LL(1)                                                        RHOMB177
      LL(1)=IT                                                           RHOMB178
   45 CONTINUE                                                           RHOMB179
      DO 50 I=1,8                                                        RHOMB180
      LSQ(1,1,I)=1H+                                                     RHOMB181
      LSQ(2,2,I)=1H+                                                     RHOMB182
      LSQ(3,3,I)=1H+                                                     RHOMB183
      LSQ(1,2,I) = LSIGN(1,I)                                            RHOMB184
      LSQ(2,1,I) = LSIGN(1,I)                                            RHOMB185
      LSQ(1,3,I) = LSIGN(3,I)                                            RHOMB186
      LSQ(3,1,I) = LSIGN(3,I)                                            RHOMB187
      LSQ(2,3,I) = LSIGN(2,I)                                            RHOMB188
      LSQ(3,2,I) = LSIGN(2,I)                                            RHOMB189
   50 CONTINUE                                                           RHOMB190
      W11 = ALA*BEAK                                                     RHOMB191
      W22 = ALB*BEBK                                                     RHOMB192
      W33 = ALC*BECK                                                     RHOMB193
      W12 = GAAK                                                         RHOMB194
      W23 = GABK                                                         RHOMB195
      W13 = GACK                                                         RHOMB196
      DO 60 I=1,8                                                        RHOMB197
   60 NSOL(I) = I                                                        RHOMB198
      PRINT 602                                                          RHOMB199
      PRINT 603,((I,(ANGLES(J,I),J=1,3)),I=1,8)                          RHOMB200
      PRINT 604,NSOL,KHA,ALA,BEAK,GAAB,(LSIGN(1,K),K=1,8),               RHOMB201
     1KHB,ALB,BEBK,GABB,(LSIGN(2,K),K=1,8)       ,KHC,ALC,BECK,GACB,    RHOMB202
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     2(LSIGN(3,K),K=1,8)                                                RHOMB203
      PRINT 605,W11,GAAB,GACB,GAAB,W22,GABB,GACB,GABB,W33               RHOMB204
      PRINT 606,NSOL,(((LSQ(I,J,K),J=1,3),K=1,8),I=1,3)                 RHOMB205
      PRINT 607,IY1,IY2,IY3,IY4                                         RHOMB206
      CALL DISPLAY(3)                                                   RHOMB207
      PRINT 608,IY1,IY2,IY1,IY3,IY2,IY4,IY3                             RHOMB208
      PRINT 609                                                         RHOMB209
      W12=-W12                                                          RHOMB210
      W23=-W23                                                          RHOMB211
      W13=-W13                                                          RHOMB212
      PRINT 607,IY5,IY6,IY7,IY8                                         RHOMB213
      CALL DISPLAY(3)                                                   RHOMB214
      PRINT 608,IY5,IY6,IY1,IY7,IY2,IY8,IY3                             RHOMB215
      PRINT 609                                                         RHOMB216
      PRINT 610                                                         RHOMB217
      RETURN                                                            RHOMB218
      END                                                               RHOMB219
      SUBROUTINE GENERAL(PHI,NN1,NN2,NN3,SS1,SS2,SS3)                   GENER  1
C  ..... PHI IS IN DEGREES.                                             GENER  2
C  NN1,NN2,NN3 ARE THE DIRECTION COSINES WITH RESPECT TO AXES 1,2,3     GENER  3
C    RESPECTIVELY OF THE ARBITRARY ROTATION AXIS C.                     GENER  4
C  SS1,SS2,SS3 ARE THE DIRECTION COSINES WITH RESPECT TO AXES 1,2,3     GENER  5
C  RESPECTIVELY OF THE STARTING DIRECTION FOR THE ROTATION ABOUT AXIS C GENER  6
C  NEITHER (NN1,NN2,NN3) NOR (SS1,SS2,SS3) NEED BE NORMALIZED.          GENER  7
      REAL M1,M2,M3,MM1,MM2,MM3,N1,N2,N3,NN1,NN2,NN3,ANGDEG(3)          GENER  8
      COMMON/PARAM/ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                  GENER  9
      COMMON/W/W11,W22,W33,W12,W23,W13                                  GENER 10
      DATA PI/3.14159265359/,TODEG/57.29577951/,TODEG2/28.64788976/,    GENER 11
     DTORAD/0.01745329252/,NSTEP/360/,NTRIES/15/                        GENER 12
C  ALA,ALB,ALC ARE THE ALPHA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. GENER 13
C  BEA,BEB,BEC ARE THE BETA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C.  GENER 14
C  GAA,GAB,GAC ARE THE GAMMA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. GENER 15
  600 FORMAT(1H1, 40X,22H.... GENERAL CASE .....,10X,6HPHI = ,1F9.4,//,  GENER 16
     A39X,28HTHE ORIGINAL PARAMETERS ARE:,/)                            GENER 17
  601 FORMAT(37X,5HALPHA,11X,4HBETA,12X,5HGAMMA,//,24X,7HAXIS A:,1F16.8,GENER 18
     B2E16.9//24X,7HAXIS B:,1F16.8,2E16.9//24X,7HAXIS C:,F16.8,2E16.9//)GENER 19
  602 FORMAT(28X, 72HTHE VECTOR (N1,N2,N3) REPRESENTING THE DIRECTION OFGENER 20
     C AXIS C IS GIVEN AS (,1F9.6,1H,1F9.6,1H,1F9.6,1H),/, 69X,31HTHIS IGENER 21
     DS NORMALIZED TO PRODUCE (,1F9.6,1H,1F9.6,1H,1F9.6,1H))            GENER 22
  603 FORMAT(100H THE VECTOR (S1,S2,S3) REPRESENTING THE STARTING DIRECTGENER 23
     EION FOR A ROTATION ABOUT AXIS C IS GIVEN AS (,1F9.6,1H,1F9.6,1H,  GENER 24
     F1F9.6,1H))                                                        GENER 25
  604 FORMAT(84H THIS VECTOR IS PROJECTED ONTO THE PLANE PERPENDICULAR TGENER 26
     GO (N1,N2,N3) AND NORMALIZED.,/,76X, 24HTHESE CORRECTIONS GIVE (,  GENER 27
     H1F9.6,1H,1F9.6,1H,1F9.6,1H),/, 40X,60HTHE STARTING-DIRECTION VECTOGENER 28
     IR (S1,S2,S3) IS NOW CHANGED TO (,1F9.6,1H,1F9.6,1H,1F9.6,1H))     GENER 29
  605 FORMAT(40X,17HBY A ROTATION OF F9.4,25H DEGREES ABOUT (N1,N2,N3)/)GENER 30
  606 FORMAT(43H THIS CHANGES THE FOLLOWING TWO PARAMETERS:,/, 35H  BETAGENER 31
     J FOR ROTATION ABOUT AXIS C = ,1E15.9,/,35H GAMMA FOR ROTATION ABOUGENER 32
     KT AXIS C = ,1E15.9,//)                                            GENER 33
  607 FORMAT(22X, 38HTHE STARTING-ANGLE ERRORS (IN DEGREES), /, 22X,    GENER 34
     L29HABOUT THE THREE ROTATION AXES,/,23X,6HAXIS A,6X,6HAXIS B,6X,   GENER 35
     M6HAXIS C)                                                         GENER 36
  608 FORMAT(3X,12HSOLUTION NO.. I2,4H... ,F9.4,3X,F9.4,3X,F9.4)        GENER 37
  609 FORMAT(/,36X, 48HTHIS SOLUTION HAS THE FOLLOWING ALPHA,BETA,GAMMA,GENER 38
     N/, 36X,41HPARAMETERS FOR THE THREE AXES OF ROTATION)              GENER 39
  610 FORMAT(/,27(5H  *  ),//,49X,27H... END OF CALCULATIONS ...)       GENER 40
  700 FORMAT(//, 65H THERE IS AN ERROR. AN ITERATIVE PROCESS DID NOT CONGENER 41
     OVERGE WITHIN , I4,11H ITERATIONS,/,36H THE VALUE OF THE NULL FUNCTGENER 42
     PIONS ARE,/, 6H E1 = ,E15.9,6H E2 = ,E15.9,6H E3 = ,E15.9,/,       GENER 43
     @18H ANGA,ANGB,ANGC = , 3E15.9,/)                                  GENER 44
 1999 FORMAT(19H ERROR IN GENERAL: ,2I6,/,(39X,3E15.9,/) )              GENER 45
      FE = PHI*TORAD                                                    GENER 46
      NSOL = 0                                                          GENER 47
      ABSTEP=PI/FLOAT(NSTEP)                                            GENER 48
      STEP=ABSTEP                                                       GENER 49
      ACCUR=STEP/10000.0                                                GENER 50
      CONV = 3.0*ABSTEP                                                 GENER 51
      PRINT 600,PHI                                                     GENER 52
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      PRINT 601,ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                    GENER 53
C     ..... NORMALIZE (NN1,NN2,NN3) TO FORM (N1,N2,N3) ...             GENER 54
      RENORM = SQRT(NN1*NN1+NN2*NN2+NN3*NN3)                           GENER 55
      IF(RENORM) 4,999                                                 GENER 56
    4 N1=NN1/RENORM                                                    GENER 57
      N2=NN2/RENORM                                                    GENER 58
      N3=NN3/RENORM                                                    GENER 59
      PRINT 602,NN1,NN2,NN3,N1,N2,N3                                   GENER 60
      PRINT 603,SS1,SS2,SS3                                            GENER 61
C     ..... PROJECT (SS1,SS2,SS3) ONTO THE PLANE PERPENDICULAR TO THE  GENER 62
C           VECTOR (N1,N2,N3) ...                                      GENER 63
      DCSN = SS1*N1+SS2*N2+SS3*N3                                      GENER 64
      SS1=SS1-DCSN*N1                                                  GENER 65
      SS2=SS2-DCSN*N2                                                  GENER 66
      SS3=SS3-DCSN*N3                                                  GENER 67
C     ..... NORMALIZE THE NEW (SS1,SS2,SS3)                            GENER 68
      RENORM = SQRT(SS1*SS1+SS2*SS2+SS3*SS3)                           GENER 69
      IF(RENORM) 5,999                                                 GENER 70
    5 SS1=SS1/RENORM                                                   GENER 71
      SS2=SS2/RENORM                                                   GENER 72
      SS3=SS3/RENORM                                                   GENER 73
C     ..... FORM (MM1,MM2,MM3) FROM (N1,N2,N3) CROSS (SS1,SS2,SS3) ... GENER 74
      MM1=N2*SS3-N3*SS2                                                GENER 75
      MM2=N3*SS1-N1*SS3                                                GENER 76
      MM3=N1*SS2-N2*SS1                                                GENER 77
C     ..... CHANGE TO A NEW STARTING DIRECTION (S1,S2,S3) WHERE S3=0.0 AND GENER 78
C           A CORRESPONDING NEW MIDDLE DIRECTION (M1,M2,M3) ...        GENER 79
      IF(MM3) 6,999,6                                                  GENER 80
    6 IF(SS3) 8,7                                                      GENER 81
    7 M1=MM1                                                           GENER 82
      M2=MM2                                                           GENER 83
      M3=MM3                                                           GENER 84
      S1=SS1                                                           GENER 85
      S2=SS2                                                           GENER 86
      S3=SS3                                                           GENER 87
      BECS=BEC                                                         GENER 88
      GACS=GAC                                                         GENER 89
      XI = 0.0                                                         GENER 90
      GO TO 18                                                         GENER 91
    8 ALMDA = SQRT(SS3*SS3+MM3*MM3)                                    GENER 92
      S1 = (SS1*MM3-SS3*MM1)/ALMDA                                     GENER 93
      S2 = (SS2*MM3-SS3*MM2)/ALMDA                                     GENER 94
      S3 = 0.0                                                         GENER 95
      M1 = (SS1*SS3+MM1*MM3)/ALMDA                                     GENER 96
      M2 = (SS2*SS3+MM2*MM3)/ALMDA                                     GENER 97
      M3 = ALMDA                                                       GENER 98
      TANXI = -SS3/MM3                                                 GENER 99
      XI = ATAN(TANXI)*TODEG                                           GENER100
      IF(MM3) 10,10,15                                                 GENER101
   10 XI = XI-SIGN(180.0,SS3)                                          GENER102
C    XI IS THE ANGLE OF ROTATION ABOUT (N1,N2,N3) TO PRODUCE (S1,S2,S3). GENER103
C     ..... NEW BETA AND GAMMA PARAMETERS FOR ROTATION ABOUT AXIS C.   GENER104
C           OLD VALUES BEC,GAC ARE ASSOCIATED WITH (SS1,SS2,SS3)...    GENER105
C           NEW VALUES BECS,GACS ARE ASSOCIATED WITH (S1,S2,S3).       GENER106
   15 BECS = (BEC*(MM3**2-SS3**2)-2.0*GAC*MM3*SS3)/(ALMDA*ALMDA)       GENER107
      GACS = (GAC*(MM3**2-SS3**2)+2.0*BEC*MM3*SS3)/(ALMDA*ALMDA)       GENER108
   18 PRINT 604,SS1,SS2,SS3,S1,S2,S3                                   GENER109
      PRINT 605,XI                                                     GENER110
      PRINT 606,BECS,GACS                                              GENER111
      ZLMDAA=SQRT(BEA**2+GAA**2)                                       GENER112
      ZLMDAB=SQRT(BEB**2+GAB**2)                                       GENER113
      ZLMDAC=SQRT(BECS**2+GACS**2)                                     GENER114
      DPLUSA = SIGN(ACOS(BEA/ZLMDAA),GAA)                              GENER115
      DPLUSB = SIGN(ACOS(BEB/ZLMDAB),GAB)                              GENER116
      DPLUSC = SIGN(ACOS(BECS/ZLMDAC),GACS)                            GENER117
      SNFE = SIN(FE)                                                   GENER118
      CSFE = COS(FE)                                                   GENER119
      SN2FE = SIN(2.0*FE)                                              GENER120
      SNFE2=SNFE**2                                                    GENER121
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      CSFE2=CSFE**2                                                     GENER122
      BEAK=BEA                                                          GENER123
      BEBK=BEB                                                          GENER124
      BECK=BECS                                                         GENER125
      GAAK=GAA                                                          GENER126
      GABK=GAB                                                          GENER127
      GACK=GACS                                                         GENER128
      CMIN = (ALA-ALB-ZLMDAB)/ZLMDAA                                    GENER129
      CMAX = (ALA-ALB+ZLMDAB)/ZLMDAA                                    GENER130
      CMIN = AMAX1(CMIN,-1.0)                                           GENER131
      CMAX = AMIN1(CMAX,+1.0)                                           GENER132
      XMAX = ACOS(CMIN)                                                 GENER133
      XMIN = ACOS(CMAX)                                                 GENER134
      IBEG = IFIX(XMIN/STEP)                                            GENER135
      IEND = IFIX(XMAX/STEP)+1                                          GENER136
      IF(IEND-IBEG) 999,999,20                                          GENER137
   20 DO 201 III=1,2                                                    GENER138
      STEP = -STEP                                                      GENER139
      PNB = +1.0                                                        GENER140
      PNC = -1.0                                                        GENER141
      DO 201 LMN=1,4                                                    GENER142
      T=PNB                                                             GENER143
      PNB=-PNC                                                          GENER144
      PNC=T                                                             GENER145
      KLL=0                                                             GENER146
      KSCH=0                                                            GENER147
      INDEX=0                                                           GENER148
      CROSS=+1.0                                                        GENER149
      DO 200 I=IBEG,IEND                                                GENER150
C  ..... INDEX = NUMBER OF STEPS IN ALLOWED REGION.                     GENER151
C  ..... KLL = 0 FORBIDDEN REGION                                       GENER152
C  ..... KLL = 1 ALLOWED REGION                                         GENER153
C  ..... KLLSV = VALUE OF KLL FOR PREVIOUS STEP. ENTERING THE DO LOOP   GENER154
C  ..... KSCH = (0,1) IF SEARCH FOR CROSSOVER (DOES NOT,DOES) OCCUR.    GENER155
C  ..... KSCHSV = VALUE OF KSCH FOR PREVIOUS STEP.                      GENER156
C  FOR THE FIRST TIME CAUSES KLLSV TO BE SET TO 0.                      GENER157
C  ..... CROSS IS LESS THAN OR EQUAL TO 0.0 ONLY IF A CROSSOVER IS TO   GENER158
C  BE SEARCHED FOR.                                                     GENER159
C  ..... FUNC = TEST FUNCTION = E3. WE SEARCH FOR THE ZERO VALUES.      GENER160
C  ..... SFUNC = LAST VALUE OF FUNC                                     GENER161
C  ..... SSFUNC = SECOND TO THE LAST VALUE OF FUNC                      GENER162
      ZTA=FLOAT(I)*STEP                                                 GENER163
      CSZTA=COS(ZTA)                                                    GENER164
      KLLSV=KLL                                                         GENER165
      KSCHSV=KSCH                                                       GENER166
      KSCH=0                                                            GENER167
      SSFUNC=SFUNC                                                      GENER168
      SFUNC=FUNC                                                        GENER169
      CSZTB=(ZLMDAA*CSZTA+ALB-ALA)/ZLMDAB                               GENER170
      IF(ABS(CSZTB)-1.0) 38,38,190                                      GENER171
   38 SNZTA = SIN(ZTA)                                                  GENER172
      CSZTC=(ZLMDAA*((2.*S1*S1-1.)*CSZTA+2.*S1*S2*SNZTA)+ALA-ALC)/ZLMDACGENER173
      IF(ABS(CSZTC)-1.0) 39,39,190                                      GENER174
C ....... ALLOWED ZONE .....                                           GENER175
   39 KLL=1                                                             GENER176
      INDEX=INDEX+1                                                     GENER177
C  ..... CALCULATE FUNC ...                                             GENER178
      SNZTB = SIGN((SQRT(1.0-CSZTB**2)),PNB)                            GENER179
      SNZTC = SIGN((SQRT(1.0-CSZTC**2)),PNC)                            GENER180
      BEAK = ZLMDAA*CSZTA                                               GENER181
      BEBK = ZLMDAB*CSZTB                                               GENER182
      BECK = ZLMDAC*CSZTC                                               GENER183
      GAAK = ZLMDAA*SNZTA                                               GENER184
      GABK = ZLMDAB*SNZTB                                               GENER185
      GACK = ZLMDAC*SNZTC                                               GENER186
      W23=(GAAK*CSFE-GABK)/SNFE                                         GENER187
      W13=(GACK+2.0*BEAK*S2*M2-GAAK*(S1*M2+S2*M1)-W23*S2*M3)/(S1*M3)    GENER188
      W33=(ALB+BEBK-(ALA+BEAK)*CSFE2+W13*SNFE)/SNFE2                    GENER189
      FUNC=ALA*(1.0-M3**2)+BEAK*(M1**2-M2**2)+2.0*GAAK*M1*M2+2.0*W23*M2*GENER190
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     FM3+2.0*W13*M1*M3+W33*M3**2-ALC+BECK                                GENER191
C  ..... IF LAST STEP WAS IN THE FORBIDDEN REGION, CHECK FOR CROSSOVER.  GENER192
      IF(KLLSV) 50,100                                                   GENER193
C  ..... IF INDEX=1, THIS IS THE FIRST STEP AND ANOTHER STEP IS TAKEN.   GENER194
C  IF FUNC=0.0, THEN THIS WILL BE DETERMINED BY THE PRODUCT SFUNC*FUNC   GENER195
   50 IF(INDEX-1) 200,200,52                                             GENER196
   52 CROSS = SFUNC*FUNC                                                 GENER197
C  ..... IF CROSS IS NEGATIVE OR ZERO, A CROSSOVER HAS OCCURED.          GENER198
      IF(CROSS) 100,100,54                                               GENER199
C  ..... INDEX MUST BE AT LEAST 3 FOR THE FOLLOWING CHECK TO BE VALID    GENER200
   54 IF(INDEX-3) 200,56,56                                              GENER201
C  ..... WE TEST TO SEE IF THE FUNCTION HAS APPROACHED TOWARD AND THEN   GENER202
C  RETREATED FROM THE FUNC=0.0 AXIS.  THERE ARE TWO CONDITIONS THAT      GENER203
C  MUST BE MET FOR THIS TO HAVE OCCURED.                                 GENER204
C  (1). (FUNC-SFUNC)*(SFUNC-SSFUNC) MUST BE LESS THAN OR EQUAL TO ZERO   GENER205
C  (2). FUNC*(FUNC-SFUNC) MUST BE GREATER THAN OR EQUAL TO ZERO.         GENER206
   56 CHECK = (FUNC-SFUNC)*(SFUNC-SSFUNC)                                GENER207
      IF(CHECK) 58,58,200                                                GENER208
   58 CHECK = FUNC*(FUNC-SFUNC)                                          GENER209
      IF(CHECK) 200,100,100                                              GENER210
C ..... ROUTINE FOR SEARCHING FOR CROSSOVER POINTS ........              GENER211
C CALCULATE THE THREE ANGLES ABOUT WHICH THE SEARCH IS TO BEGIN          GENER212
C  ..... ANGA,ANGB,ANGC ARE THE (DOUBLE)-STARTING-ANGLE-SHIFTS FOR      GENER213
C  ROTATIONS ABOUT AXES A,B,C RESPECTIVELY.                              GENER214
  100 KSCH=1                                                             GENER215
      ANGA = DPLUSA-ZTA                                                  GENER216
      ANGB = DPLUSB-SIGN(ACOS(CSZTB),PNB)                                GENER217
      ANGC = DPLUSC-SIGN(ACOS(CSZTC),PNC)                                GENER218
      JFLAG=0                                                            GENER219
      GO TO 112                                                          GENER220
  110 ANGA=ANGA+DELA                                                     GENER221
      ANGB=ANGB+DELB                                                     GENER222
      ANGC=ANGC+DELC                                                     GENER223
  112 CSA=COS(ANGA)                                                      GENER224
      CSB=COS(ANGB)                                                      GENER225
      CSC=COS(ANGC)                                                      GENER226
      SNA=SIN(ANGA)                                                      GENER227
      SNB=SIN(ANGB)                                                      GENER228
      SNC=SIN(ANGC)                                                      GENER229
      BEAK=BEA*CSA+GAA*SNA                                               GENER230
      BEBK=BEB*CSB+GAB*SNB                                               GENER231
      BECK=BECS*CSC+GACS*SNC                                             GENER232
      GAAK=GAA*CSA-BEA*SNA                                               GENER233
      GABK=GAB*CSB-BEB*SNB                                               GENER234
      GACK=GACS*CSC-BECS*SNC                                             GENER235
      W11=ALA+BEAK                                                       GENER236
      W22=ALA-BEAK                                                       GENER237
      W12=GAAK                                                           GENER238
      W23=(GAAK*CSFE-GABK)/SNFE                                          GENER239
      W13=(GACK+2.0*BEAK*S2*M2-GAAK*(S1*M2+S2*M1)-W23*S2*M3)/(S1*M3)     GENER240
      W33=(ALB+BEBK-(ALA+BEAK)*CSFE2+W13*SN2FE)/SNFE2                    GENER241
      E1=ALB-BEBK-ALA+BEAK                                               GENER242
      E2=ALA+BEAK*(2.0*S1**2-1.0)+2.0*GAAK*S1*S2-ALC-BECK                GENER243
      E3=ALA*(1.0-M3**2)+BEAK*(M1**2-M2**2)+2.0*GAAK*M1*M2+2.0*W23*M2*M3GENER244
     E+2.0*W13*M1*M3+W33*M3**2-ALC+BECK                                  GENER245
      BB=E1/GABK                                                         GENER246
      BBP=GAAK/GABK                                                      GENER247
      CC=E2/GACK                                                         GENER248
      CCP=(GAAK*(2.0*S1**2-1.0)-2.0*BEAK*S1*S2)/GACK                     GENER249
      PP=BEBK*BB/SNFE                                                    GENER250
      PPP=(BEBK*BBP-BEAK*CSFE)/SNFE                                      GENER251
      QQ=-(BECK*CC+PP*S2*M3)/(S1*M3)                                     GENER252
      QQP=(-BECK*CCP+2.*GAAK*S2*M2+BEAK*(S1*M2+S2*M1)-PPP*S2*M3)/(S1*M3)GENER253
      RR=(E1+QQ*SN2FE)/SNFE2                                             GENER254
      RRP=GAAK+(2.0*QQP*CSFE/SNFE)                                       GENER255
      F1 = -E3-E2-RR*M3**2-2.0*PP*M2*M3-2.0*QQ*M1*M3                     GENER256
      F2 = GAAK*(M1**2+S1**2-M2**2-S2**2)-2.0*BEAK*(M1*M2+S1*S2)+        GENER257
     F RRP*M3**2+2.0*PPP*M2*M3+2.0*QQP*M1*M3                             GENER258
      DELA=F1/F2                                                         GENER259
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      DELB=BB+BBP*DELA                                                  GENER260
      DELC=CC+CCP*DELA                                                  GENER261
      XXA = ABS(DELA)                                                   GENER262
      IF(JFLAG) 114,114,119                                             GENER263
  114 IF(XXA-CONV) 119,119,115                                          GENER264
  115 IF(CROSS) 119,119,200                                             GENER265
  119 JFLAG=JFLAG+1                                                     GENER266
      IF(JFLAG-NTRIES) 120,120,195                                      GENER267
  120 XXB = ABS(DELB)                                                   GENER268
      XXC = ABS(DELC)                                                   GENER269
      XX = AMAX1(XXA,XXB,XXC)                                           GENER270
      IF(XX-ACCUR) 130,130,123                                          GENER271
  123 IF(XXA-ABSTEP) 125,125,124                                        GENER272
  124 DELA = SIGN(ABSTEP,DELA)                                          GENER273
  125 IF(XXB-ABSTEP) 127,127,126                                        GENER274
  126 DELB = SIGN(ABSTEP,DELB)                                          GENER275
  127 IF(XXC-ABSTEP) 110,110,128                                        GENER276
  128 DELC = SIGN(ABSTEP,DELC)                                          GENER277
      GO TO 110                                                         GENER278
  130 ANGDEG(1) = ANGA*TODEG2                                           GENER279
      ANGDEG(2) = ANGB*TODEG2                                           GENER280
      ANGDEG(3) = ANGC*TODEG2                                           GENER281
C CHANGE THE STARTING-ANGLE SHIFT SO THAT ITS MAGNITUDE IS LESS THAN 90 GENER282
C DEGREES. TO ADD OR SUBTRACT 180 DEGREES DOES NOT AFFECT THE SOLUTION. GENER283
      DO 140 K=1,3                                                      GENER284
  136 XZ = ABS(ANGDEG(K))-90.0                                          GENER285
      IF(XZ) 140,140,137                                                GENER286
  137 ANGDEG(K) = ANGDEG(K)-SIGN(180.0,ANGDEG(K))                       GENER287
      GO TO 136                                                         GENER288
  140 CONTINUE                                                          GENER289
      NSOL=NSOL+1                                                       GENER290
      PRINT 607                                                         GENER291
      PRINT 608,NSOL,ANGDEG                                             GENER292
      PRINT 609                                                         GENER293
      PRINT 601,ALA,BEAK,GAAK,ALB,BEBK,GABK,ALC,BECK,GACK               GENER294
      CALL DISPLAY(4)                                                   GENER295
      GO TO 200                                                         GENER296
C  ..... FORBIDDEN ZONE ... IF LAST STEP WAS IN ALLOWED ZONE AND A      GENER297
C  CROSSOVER SEARCH WAS NOT PERFORMED, THEN CHECK FOR CROSSOVER POINT   GENER298
C  AFTER RESETTING THE PREVIOUS VALUES OF ZTA,CSZTA,CSZTB,CSZTC.        GENER299
  190 INDEX=0                                                           GENER300
      KLL=0                                                             GENER301
      IF(KLLSV) 192,200                                                 GENER302
  192 IF(KSCHSV) 200,193                                                GENER303
  193 ZTA=ZTA-STEP                                                      GENER304
      CSZTA=COS(ZTA)                                                    GENER305
      SNZTA = SIN(ZTA)                                                  GENER306
      CSZTB=(ZLMDAA*CSZTA+ALB-ALA)/ZLMDAB                               GENER307
      CSZTC=(ZLMDAA*((2.*S1*S1-1.)*CSZTA+2.*S1*S2*SNZTA)+ALA-ALC)/ZLMDACGENER308
      GO TO 100                                                         GENER309
C ..... NO CROSSOVER HAS BEEN FOUND. IF CROSS IS LESS THAN 0.0, ERROR  GENER310
  195 IF(CROSS) 197,197,200                                             GENER311
  197 CROSS=+1.0                                                        GENER312
      PRINT 700,NTRIES,E1,E2,E3,ANGA,ANGB,ANGC                          GENER313
  200 CONTINUE                                                          GENER314
  201 CONTINUE                                                          GENER315
      PRINT 610                                                         GENER316
      RETURN                                                            GENER317
  999 PRINT 1999,IREG,IEND,RENORM,NN1,NN2,NN3,SS1,SS2,SS3,MM1,MM2,MM3,  GENER318
     PXMIN,XMAX,CMIN,CMAX,STEP,ZLMDAA,ZLMDAB,ZLMDAC,DPLUSA,DPLUSB,DPLUSCGENER319
      RETURN                                                            GENER320
      END                                                               GENER321
      SUBROUTINE DISPLAY(INDEX)                                         DISPL  1
      DIMENSION W(3,3),R(3,3),RA(3,3),EIG(3)                            DISPL  2
      COMMON/W/W11,W22,W33,W12,W23,W13                                  DISPL  3
      DATA TORAD/57.29577951/                                           DISPL  4
  100 FORMAT(20X,16HTHE W TENSOR IS:,2X,3(E16.9,1X),//,38X,3(E16.9,1X), DISPL  5
     A//,38X,3(E16.9,1X),/)                                             DISPL  6
  101 FORMAT(13X, 117HEACH OF THE PRINCIPAL VALUES (WHICH ARE THE SQUAREDISPL  7
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     8 ROOTS OF THE EIGENVALUES) HAS A PRINCIPAL AXIS ASSOCIATED WITH ITDISPL  8
     C., /, 13X,118HTHE DIRECTIONS OF EACH PRINCIPAL AXIS ARE GIVEN BY TDISPL  9
     DHE PROJECTIONS OF THIS AXIS (I.E. DIRECTION COSINES) ON THE 3 AXESDISPL 10
     E, /, 13X,110HOF THE ORIGINAL COORDINATE SYSTEM, AND THE ANGLE BETWDISPL 11
     FEEN THIS PRINCIPAL AXIS AND THE 3 COORDINATE SYSTEM AXES., /)     DISPL 12
  102 FORMAT( 69X,25HDIRECTION COSINES BETWEEN, 8X,27HANGLES (IN DEGREESDISPL 13
     G) BETWEEN, /, 56X,9HPRINCIPAL,4X,22HTHE PRINCIPAL AXIS AND,11X,   DISPL 14
     H22HTHE PRINCIPAL AXIS AND,/,56X,6HVALUES,8X,6HAXIS 1,4X,6HAXIS 2, DISPL 15
     I4X,6HAXIS 3,7X,6HAXIS 1,5X,6HAXIS 2,5X,6HAXIS 3 )                 DISPL 16
  103 FORMAT(3(/,28X,22HPRINCIPAL AXIS NUMBER ,I1,2H :,F13.9,2X,F8.6,2X,DISPL 17
     JF8.6,2X,F8.6,6H    ,  ,F8.4,3X,F8.4,3X,F8.4,/),/)                 DISPL 18
      W(1,1) = W11                                                      DISPL 19
      W(1,2) = W12                                                      DISPL 20
      W(1,3) = W13                                                      DISPL 21
      W(2,1) = W12                                                      DISPL 22
      W(2,2) = W22                                                      DISPL 23
      W(2,3) = W23                                                      DISPL 24
      W(3,1) = W13                                                      DISPL 25
      W(3,2) = W23                                                      DISPL 26
      W(3,3) = W33                                                      DISPL 27
      IF(INDEX-3) 1,2,1                                                 DISPL 28
    1 PRINT 100,((W(I,J),J=1,3),I=1,3)                                  DISPL 29
C  ..... DIAG1 RETURNS THE EIGENVECTORS IN THE COLUMNS OF R ...          DISPL 30
    2 CALL DIAG1(3,1,1.0E-8,W,R,EIG)                                    DISPL 31
      DO 3 I=1,3                                                        DISPL 32
    3 EIG(I) = SQRT(EIG(I))                                             DISPL 33
      DO 10 I=1,3                                                       DISPL 34
      DO 10 J=1,3                                                       DISPL 35
      XX = R(I,J)                                                       DISPL 36
      YY = ABS(XX)                                                      DISPL 37
      IF(YY-1.0) 10,10,8                                                DISPL 38
    8 XX = SIGN(1.0,XX)                                                 DISPL 39
   10 RA(I,J) = ACOS(XX)*TORAD                                          DISPL 40
      PRINT 101                                                         DISPL 41
      PRINT 102                                                         DISPL 42
C  .....THE EIGENVECTORS ARE PRINTED OUT IN ROWS ...                    DISPL 43
      PRINT 103,((I,EIG(I),(R(J,I),J=1,3),(RA(J,I),J=1,3)),I=1,3)       DISPL 44
      RETURN                                                            DISPL 45
      END                                                               DISPL 46
      SUBROUTINE DIAG1(NSIZE,IFLAG,ERROR,A,R,EIG)                       DIAG   1
      DIMENSION A(3,3),R(3,3),TT(3,3),EIG(3)                            DIAG   2
C INPUT: NSIZE,IFLAG,ERROR,A(NZ,NZ).    OUTPUT: R(NZ,NZ),EIG(NZ).        DIAG   3
C NEED ONLY THE TOP HALF AND DIAGONAL OF MATRIX A(NSIZE,NSIZE).          DIAG   4
C DIAG1 DIAGONALIZES REAL SYMMETRIC MATRICES WHOSE DIMENSIONS ARE LESS   DIAG   5
C THAN OR EQUAL TO THOSE IN THE DIMENSION STATEMENT. IT DOES NOT DESTROYDIAG   6
C INPUT. IT USES THE JACOBI METHOD WITH A 4-SQUARE ROOT METHOD FOR       DIAG   7
C EVALUATING COS AND SIN. A SINGLE-PRECISION SQUARE ROOT IS USED. IT     DIAG   8
C SEARCHES FOR ABSOLUTE VALUES LESS THAN RHO WHICH IS PROGRESSIVELY      DIAG   9
C REDUCED. IF IT IS TOLD TO DOUBLE-CHECK THE ANSWER, IT DOES SO BY       DIAG  10
C SEEING IF THE ABSOLUTE VALUE OF ANY OFF-DIAGONAL ELEMENT IS GREATER    DIAG  11
C THAN ERROR. IF SO, DIAG1 CONTINUES THE JACOBI PROCESS.                 DIAG  12
C  NSIZE, THE SIZE OF THE MATRIX WHICH MUST BE .LE. NZ, WHERE NZ IS THE  DIAG  13
C    DIMENSION USED IN A(NZ,NZ),R(NZ,NZ),TT(NZ,NZ),EIG(NZ).              DIAG  14
C  IFLAG=(0,1), (NO,YES) THE DIAGONALIZATION SHOULD BE DOUBLE-CHECKED.   DIAG  15
C  ERROR, THE LARGEST ALLOWED ABSOULUTE VALUE OF AN OFF-DIAGONAL ELEMENTDIAG  16
C    IN THE MATRIX FORMED BY MULTIPLYING RAR(-1).                        DIAG  17
C  A(NZ,NZ), THE INPUT MATRIX CONTAINING A(NSIZE,NSIZE) WHICH IS THE     DIAG  18
C    REAL SYMMETRIC MATRIX TO BE DIAGONALIZED.                           DIAG  19
C  R(NZ,NZ) CONTAINS R(NSIZE,NSIZE) WHICH IS THE OUTPUT UNITARY MATRIX   DIAG  20
C    WITH THE EIGENVECTORS IN THE ROWS.                                  DIAG  21
C  EIG(NZ) CONTAINS EIG(NSIZE) WHICH IS THE OUTPUT EIGENVALUES. THE NTH  DIAG  22
C    EIGENVALUE IN EIG HAS ITS EIGENVECTOR IN THE NTH ROW OF R.          DIAG  23
C MATRIX TT ONLY NEEDED IF THE DIAGONALIZATION IS TO BE DOUBLE-CHECKED.  DIAG  24
C .... DIMENSIONIZE A,R,TT AS (NZ,NZ) AND EIG AS (NZ) WHERE NZ.GE.NSIZE  DIAG  25
      BIG=ABS(A(1,2)) $ NSZ1=NSIZE-1 $ ERR1=0.8*ERROR                   DIAG  26
      DO 10 J=1,NSIZE                                                   DIAG  27
      IREG=J+1 $ R(J,J)=1.0 $ EIG(J)=A(J,J)                             DIAG  28
      IF(J-NSIZE) 5,12,12                                               DIAG  29
    5 DO 10 I=IREG,NSIZE                                                DIAG  30
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C TAKE THE UPPER-HALF ELEMENTS AND PUT THEM IN THE LOWER HALF. THE LOWERDIAG  31
C HALF IS DESTROYED BY BEING DIAGONALIZED. SET UP R AS A UNIT MATRIX    DIAG  32
      ATM=A(J,I) $ A(I,J)=ATM $ R(I,J)=0.0 $ R(J,I)=0.0                 DIAG  33
      BIG=AMAX1(BIG,ABS(A(J,I)))                                        DIAG  34
   10 CONTINUE                                                          DIAG  35
   12 IF(BIG-ERROR) 13,14,14                                            DIAG  36
   13 RETURN                                                            DIAG  37
   14 RHO = BIG                                                         DIAG  38
   15 RHO = 0.1*RHO                                                     DIAG  39
   20 IND = 0                                                           DIAG  40
C SEARCH FOR THE ELEMENTS GREATER THAN RHO                              DIAG  41
      DO 300 IP=1,NSZ1                                                  DIAG  42
      IBEG=IP+1                                                         DIAG  43
      DO 300 IQ=IBEG,NSIZE                                              DIAG  44
      XX = A(IQ,IP)                                                     DIAG  45
      YY = ABS(XX)                                                      DIAG  46
      IF(YY-RHO) 300,40,40                                              DIAG  47
C CALCULATE CX AND SX BY THE ALGEBRAIC 4-SQUARE ROOT METHOD             DIAG  48
   40 APQ = XX                                                          DIAG  49
      U = 0.5*(EIG(IP)-EIG(IQ))                                         DIAG  50
      W = -APQ/SQRT(APQ**2+U**2)                                        DIAG  51
      IF(U) 41,42,42                                                    DIAG  52
   41 W = -W                                                            DIAG  53
   42 SX = W/(SQRT(2.0*(1.0+SQRT(1.0-W**2))))                           DIAG  54
      CX = SQRT(1.0-SX**2)                                              DIAG  55
      L=0                                                               DIAG  56
   90 L=L+1                                                             DIAG  57
      IF(L-NSIZE) 92,92,200                                             DIAG  58
   92 IF(L-IQ) 94,90,94                                                 DIAG  59
   94 IF(L-IP) 100,90,110                                               DIAG  60
  100 T1=A(IP,L) $ GO TO 120                                            DIAG  61
  110 T1=A(L,IP)                                                        DIAG  62
  120 IF(L-IQ) 130,140,140                                              DIAG  63
  130 T2=A(IQ,L) $ A(IQ,L)=T1*SX+T2*CX $ GO TO 150                      DIAG  64
  140 T2=A(L,IQ) $ A(L,IQ)=T1*SX+T2*CX                                  DIAG  65
  150 IF(L-IP) 160,180,180                                              DIAG  66
  160 A(IP,L)=T1*CX-T2*SX $ GO TO 90                                    DIAG  67
  180 A(L,IP)=T1*CX-T2*SX $ GO TO 90                                    DIAG  68
  200 APP=EIG(IP) $ AQQ=EIG(IQ) $ A(IQ,IP)=0.0                          DIAG  69
      EIG(IP)=APP*CX*CX+AQQ*SX*SX-2.0*APQ*SX*CX                         DIAG  70
      EIG(IQ)=APP*SX*SX+AQQ*CX*CX+2.0*APQ*SX*CX                         DIAG  71
      DO 250 I=1,NSIZE                                                  DIAG  72
      T1=R(I,IP) $ T2=R(I,IQ)                                           DIAG  73
      R(I,IP)=T1*CX-T2*SX                                               DIAG  74
  250 R(I,IQ)=T1*SX+T2*CX                                               DIAG  75
      IND=IND+1                                                         DIAG  76
  300 CONTINUE                                                          DIAG  77
      IF(IND) 305,305,20                                                DIAG  78
  305 IF(RHO-ERR1) 307,307,15                                           DIAG  79
C IF FLAG=1 DOUBLE-CHECK BY MULTIPLYING RAR(-1)                         DIAG  80
  307 IF(IFLAG-1) 308,309,308                                           DIAG  81
  308 RETURN                                                            DIAG  82
  309 DO 330 I=1,NSIZE $ DO 330 J=1,NSIZE                               DIAG  83
      TOT=0.0                                                           DIAG  84
      DO 320 L=1,NSIZE                                                  DIAG  85
      IF(L-I) 310,315,315                                               DIAG  86
  310 EL=A(L,I) $ GO TO 320                                             DIAG  87
  315 EL=A(I,L)                                                         DIAG  88
  320 TOT=TOT+EL*R(L,J)                                                 DIAG  89
  330 TT(I,J)=TOT                                                       DIAG  90
      DO 350 I=1,NSIZE $ DO 350 J=1,NSIZE                               DIAG  91
      VALUE=0.0                                                         DIAG  92
      DO 340 L=1,NSIZE                                                  DIAG  93
  340 VALUE=VALUE+R(L,I)*TT(L,J)                                        DIAG  94
      IF(I.EQ.J) 345,349                                                DIAG  95
  345 EIG(I)=VALUE  $ GO TO 350                                         DIAG  96
  349 IF(ABS(VALUE).GT.ERROR) GO TO 355                                 DIAG  97
  350 CONTINUE                                                          DIAG  98
      RETURN                                                            DIAG  99
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C IF OFF-DIAGONAL ELEMENTS ARE TOO LARGE, CALCULATE A AND CONTINUE      DIAG 100
  355 DO 370 J=1,NSIZE $ DO 370 I=J,NSIZE                               DIAG 101
      TOT=0.0                                                           DIAG 102
      DO 360 L=1,NSIZE                                                  DIAG 103
  360 TOT=TOT+R(L,I)*TT(L,J)                                            DIAG 104
      IF(I-J) 364,362,364                                               DIAG 105
  362 EIG(J)=TOT $ GO TO 370                                            DIAG 106
  364 A(I,J)=TOT                                                        DIAG 107
  370 CONTINUE                                                          DIAG 108
      ERR1 = 0.5*ERR1                                                   DIAG 109
      GO TO 20                                                          DIAG 110
      END                                                               DIAG 111
      SUBROUTINE PARAM(INDEX,G,R,FE,SI,N1,N2,N3,KSTART,S1,S2,S3,ABG)    PARAM  1
      REAL G(3),R(3,3),GG(2),THETA(2),N(3),S(3),N1,N2,N3,ABG(9)         PARAM  2
C THIS SUBROUTINE CALCULATES THE ALPHA,BETA,GAMMA PARAMETERS FOR THREE  PARAM  3
C ROTATIONS OF A G-TENSOR.                                              PARAM  4
C IT DOES THIS FOR THE COPLANAR,MONOCLINIC,ORTHORHOMBIC,AND GENERAL CASEPARAM  5
C  INPUT: INDEX,G(3),R(3,3)                                            PARAM  6
C  OPTIONAL INPUT: FE,SI,N1,N2,N3,KSTART,S1,S2,S3                       PARAM  7
C  OUTPUT: ABG(9) WHICH CONTAINS 9 VALUES IN THE FOLLOWING ORDER: ALA,  PARAM  8
C     BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                                   PARAM  9
C  ALA,ALB,ALC ARE THE ALPHA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. PARAM 10
C  BEA,BEB,BEC ARE THE BETA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C.  PARAM 11
C  GAA,GAB,GAC ARE THE GAMMA PARAMETERS FOR ROTATIONS ABOUT AXES A,B,C. PARAM 12
C   INDEX=(1,2,3,4) FOR THE (COPLANAR,MONOCLINIC,ORTHORHOMBIC,GENERAL)  PARAM 13
C     CASES RESPECTIVELY.                                               PARAM 14
C  G(3) CONTAINS THE 3 PRINCIPLE G-VALUES.                              PARAM 15
C  R(3,3) CONTAINS THE 3 EIGENVECTORS IN ROWS. IT IS THE UNITARY MATRIX PARAM 16
C     IN R(-1)*G(DIAGONAL)*R = W.                                       PARAM 17
C  FE IS THE ANGLE PHI(IN RADIANS) ABOUT AXIS 3 WHICH DETERMINES THE    PARAM 18
C     DIRECTION OF THE 2ND ROTATION(AXIS B) IN THE COPLANAR,MONOCLINIC, PARAM 19
C     AND GENERAL CASES.                                                PARAM 20
C  SI IS THE ANGLE PSI(IN RADIANS) ABOUT AXIS 3 WHICH DETERMINES THE    PARAM 21
C     DIRECTION OF THE 3RD ROTATION (AXIS C) IN THE COPLANAR CASE.      PARAM 22
C N1,N2,N3 ARE THE 3 COMPONENTS OF A VECTOR SPECIFYING THE DIRECTION OF PARAM 23
C     THE 3RD AXIS OF ROTATION(AXIS C) FOR THE GENERAL CASE. THIS VECTORPARAM 24
C     NEED NOT BE OF UNIT LENGTH.                                       PARAM 25
C S1,S2,S3 ARE THE 3 COMPONENTS OF A VECTOR SPECIFYING THE STARTING     PARAM 26
C     DIRECTION (WHEN THETA=ZERO DEGREES) FOR THE 3RD AXIS OF ROTATION  PARAM 27
C     (AXIS C) FOR THE GENERAL CASE.                                    PARAM 28
C     THESE VALUES NEED NOT BE SPECIFIED.                               PARAM 29
C  KSTART = (1,0) WHEN,FOR THE GENERAL CASE, S1,S2,S3 (ARE,ARE NOT)     PARAM 30
C     SPECIFIED.                                                        PARAM 31
C  N(3) IS A UNIT VECTOR ABOUT WHICH THE MAGNETIC FIELD IS ROTATED.     PARAM 32
C  S(3) IS A UNIT VECTOR THAT INDICATES THE STARTING DIRECTION (WHEN    PARAM 33
C     THETA=ZERO DEGREES).                                              PARAM 34
C  M(3) IS A UNIT VECTOR INDICATING THE MIDDLE DIRECTION (WHEN THETA =  PARAM 35
C     90 DEGREES).                                                      PARAM 36
C  GG(2) AND THETA(2) ARE NOT USED BUT ARE NEEDED AS F.P.S IN ALBEGA.   PARAM 37
C     ABG(9) CONTAINS THE 9 ALPHA,BETA,GAMMA PARAMETERS IN THE ORDER:   PARAM 38
C     ALA,BEA,GAA,ALB,BEB,GAB,ALC,BEC,GAC                               PARAM 39
C .... SUBROUTINE REQUIRES THE SUBROUTINE ALBEGA .....                  PARAM 40
  999 FORMAT(//,17H ERROR IN PARAM:,2I6,(3X,6E15.8,/))                  PARAM 41
      ICHECK = (INDEX-1)*(4-INDEX)                                      PARAM 42
      IF(ICHECK) 199,5,5                                                PARAM 43
    5 IADD = 1                                                          PARAM 44
      KEY = 1                                                           PARAM 45
      JZGO = 2*(INDEX-1)                                                PARAM 46
      N(1) = 0.0                                                        PARAM 47
      N(2) = 0.0                                                        PARAM 48
      N(3) = 1.0                                                        PARAM 49
      S(1) = 1.0                                                        PARAM 50
      S(2) = 0.0                                                        PARAM 51
      S(3) = 0.0                                                        PARAM 52
      GO TO 100                                                         PARAM 53
C  ..... COPLANAR CASE .....                                            PARAM 54
   11 SNFE = SIN(FE)                                                    PARAM 55
      CSFE = COS(FE)                                                    PARAM 56
      SNSI = SIN(SI)                                                    PARAM 57
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      CSSI = COS(SI)                                                    PARAM 58
      N(1) = SNFE                                                       PARAM 59
      N(2) = 0.0                                                        PARAM 60
      N(3) = CSFE                                                       PARAM 61
      S(1) = CSFE                                                       PARAM 62
      S(2) = 0.0                                                        PARAM 63
      S(3) = -SNFE                                                      PARAM 64
      GO TO 100                                                         PARAM 65
   12 N(1) = SNSI                                                       PARAM 66
      N(2) = 0.0                                                        PARAM 67
      N(3) = CSSI                                                       PARAM 68
      S(1) = CSSI                                                       PARAM 69
      S(2) = 0.0                                                        PARAM 70
      S(3) = -SNSI                                                      PARAM 71
      GO TO 100                                                         PARAM 72
C     ..... MONOCLINIC CASE .....                                       PARAM 73
   21 SNFE = SIN(FE)                                                    PARAM 74
      CSFE = COS(FE)                                                    PARAM 75
      N(1) = SNFE                                                       PARAM 76
      N(2) = 0.0                                                        PARAM 77
      N(3) = CSFE                                                       PARAM 78
      S(1) = CSFE                                                       PARAM 79
      S(2) = 0.0                                                        PARAM 80
      S(3) = -SNFE                                                      PARAM 81
      GO TO 100                                                         PARAM 82
   22 N(1) = 0.0                                                        PARAM 83
      N(2) = 1.0                                                        PARAM 84
      N(3) = 0.0                                                        PARAM 85
      S(1) = 0.0                                                        PARAM 86
      S(2) = 0.0                                                        PARAM 87
      S(3) = 1.0                                                        PARAM 88
      GO TO 100                                                         PARAM 89
C     ..... ORTHORHOMBIC CASE .....                                     PARAM 90
   31 N(1) = 1.0                                                        PARAM 91
      N(2) = 0.0                                                        PARAM 92
      N(3) = 0.0                                                        PARAM 93
      S(1) = 0.0                                                        PARAM 94
      S(2) = 1.0                                                        PARAM 95
      S(3) = 0.0                                                        PARAM 96
      GO TO 100                                                         PARAM 97
   32 N(1) = 0.0                                                        PARAM 98
      N(2) = 1.0                                                        PARAM 99
      N(3) = 0.0                                                        PARAM100
      S(1) = 0.0                                                        PARAM101
      S(2) = 0.0                                                        PARAM102
      S(3) = 1.0                                                        PARAM103
      GO TO 100                                                         PARAM104
C     ..... GENERAL CASE .....                                          PARAM105
   41 SNFE = SIN(FE)                                                    PARAM106
      CSFE = COS(FE)                                                    PARAM107
      N(1) = SNFE                                                       PARAM108
      N(2) = 0.0                                                        PARAM109
      N(3) = CSFE                                                       PARAM110
      S(1) = CSFE                                                       PARAM111
      S(2) = 0.0                                                        PARAM112
      S(3) = -SNFE                                                      PARAM113
      GO TO 100                                                         PARAM114
   42 RN = SQRT(N1**2+N2**2+N3**2)                                      PARAM115
      IF(RN) 199,199,43                                                 PARAM116
   43 N(1) = N1/RN                                                      PARAM117
      N(2) = N2/RN                                                      PARAM118
      N(3) = N3/RN                                                      PARAM119
      IF(KSTART-1) 44,50,44                                             PARAM120
   44 DN = SQRT(N(1)**2+N(2)**2)                                        PARAM121
      IF(DN) 199,199,45                                                 PARAM122
   45 S(1) = N(2)/DN                                                    PARAM123
      S(2) = -N(1)/DN                                                   PARAM124
      S(3) = 0.0                                                        PARAM125
      GO TO 100                                                         PARAM126
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   50 RN=SQRT(S1*S1+S2*S2+S3*S3)                                          PARAM127
      IF(RN) 199,199,55                                                   PARAM128
   55 S(1) = S1/RN                                                        PARAM129
      S(2) = S2/RN                                                        PARAM130
      S(3) = S3/RN                                                        PARAM131
  100 CALL ALBEGA(G,R,N,S,AL,BE,GA,GG,THETA)                              PARAM132
      ABG(KEY) = AL                                                       PARAM133
      ABG(KEY+1) = BE                                                     PARAM134
      ABG(KEY+2) = GA                                                     PARAM135
      IF(IADD-3) 102,104,104                                              PARAM136
  102 KEY = KEY+3                                                         PARAM137
      IADD = IADD+1                                                       PARAM138
      JZGO = JZGO+1                                                       PARAM139
      GO TO (11,12,21,22,31,32,41,42) JZGO                                PARAM140
  104 RETURN                                                              PARAM141
  199 PRINT 999,INDEX,KSTART,N1,N2,N3,S1,S2,S3,FE,SI,RN,DN,N,S,G,R,GG,    PARAM142
     PTHETA,ABG                                                           PARAM143
      END                                                                 PARAM144
      SUBROUTINE ALBEGA(G,R,N,S,AL,BE,GA,GG,THETA)                        ALBEG  1
      REAL G(3),R(3,3),N(3),S(3),M(3),GG(2),THETA(2),W(3,3)               ALBEG  2
      DATA TORAD/.01745329251994/                                         ALBEG  3
C THIS SUBROUTINE CALCULATES THE ALPHA,BETA,GAMMA PARAMETERS FOR A        ALBEG  4
C SPECIFIC ROTATION OF A G-TENSOR ABOUT AN ARBITRARY AXIS.                ALBEG  5
C  G(3) CONTAINS THE 3 PRINCIPLE G-VALUES.                                ALBEG  6
C INPUT: G,R,N,S     OUTPUT: AL,BE,GA,GG,THETA                            ALBEG  7
C  R(3,3) CONTAINS THE 3 EIGENVECTORS IN ROWS. IT IS THE UNITARY MATRIX   ALBEG  8
C     IN R(-1)*G(DIAGONAL)*R = W.                                         ALBEG  9
C  S(3) IS A UNIT VECTOR THAT INDICATES THE STARTING DIRECTION (WHEN      ALBEG 10
C     THETA=ZERO DEGREES).                                                ALBEG 11
C  M(3) IS A UNIT VECTOR INDICATING THE MIDDLE DIRECTION (WHEN THETA =    ALBEG 12
C     90 DEGREES).                                                        ALBEG 13
C  GG(2) CONTAINS RESPECTIVELY THE MAXIMUM AND MINIMUM VALUES OF G.       ALBEG 14
C  THETA(2) CONTAINS THE ANGLES (IN DEGREES) WHICH CORRESPOND TO THE      ALBEG 15
C     VALUES IN GG(2) RESPECTIVELY.                                       ALBEG 16
C  AL,BE,GA ARE THE ALPHA,BETA,GAMMA VALUES CALCULATED FOR THIS ROTATION  ALBEG 17
C THEY ARE THEN USED TO CALCULATE GMAX,GMIN AND THE CORRESPONDING ANGLES  ALBEG 18
C WITH THESE VALUES, ALPHA,BETA,GAMMA ARE RECALCULATED AND COMPARED WITH  ALBEG 19
C THEIR VALUES OF THE 1ST CALCULATION. IF THE FRACTIONAL CHANGE OF ANY    ALBEG 20
C OF THE 3 PARAMETERS IS GREATER THAN 1.0E-9, IT WILL PRINT EVERYTHING.   ALBEG 21
  199 FORMAT(17H ERROR IN ALBEGA:, /, (2X,6E15.9,/))                      ALBEG 22
      M(1) = N(2)*S(3)-N(3)*S(2)                                          ALBEG 23
      M(2) = N(3)*S(1)-N(1)*S(3)                                          ALBEG 24
      M(3) = N(1)*S(2)-N(2)*S(1)                                          ALBEG 25
      DO 10 I=1,3                                                         ALBEG 26
      DO 10 J=1,3                                                         ALBEG 27
      W(I,J) = 0.0                                                        ALBEG 28
      DO 10 K=1,3                                                         ALBEG 29
   10 W(I,J) = W(I,J)+(G(K)**2)*R(K,I)*R(K,J)                             ALBEG 30
      AL = 0.0                                                            ALBEG 31
      BE = 0.0                                                            ALBEG 32
      GA = 0.0                                                            ALBEG 33
      DO 20 I=1,3                                                         ALBEG 34
      DO 20 J=1,3                                                         ALBEG 35
      AL = AL+0.5*(W(I,J)*(S(I)*S(J)+M(I)*M(J)))                          ALBEG 36
      BE = BE+0.5*(W(I,J)*(S(I)*S(J)-M(I)*M(J)))                          ALBEG 37
      GA = GA+W(I,J)*S(I)*M(J)                                            ALBEG 38
   20 CONTINUE                                                            ALBEG 39
      IF(BE) 30,25                                                        ALBEG 40
   25 IF(GA) 99,28                                                        ALBEG 41
C IF BE=0.0 AND GA=0.0, THEN GG(1)=GG(2)=AL AND THETA=ANYTHING            ALBEG 42
   28 GG(1) = AL                                                          ALBEG 43
      GG(2) = AL                                                          ALBEG 44
      THE = 0.0                                                           ALBEG 45
      GO TO 40                                                            ALBEG 46
   30 THE=0.5*ATAN(GA/BE)                                                 ALBEG 47
   35 CS = COS(2.0*THE)                                                   ALBEG 48
      SN = SIN(2.0*THE)                                                   ALBEG 49
      ADD = BE*CS+GA*SN                                                   ALBEG 50
      GG(1) = SQRT(AL+ADD)                                                ALBEG 51
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      GG(2) = SQRT(AL-ADD)                                              ALBEG 52
      AL1 = 0.5*(GG(1)**2+GG(2)**2)                                     ALBEG 53
      WIK = GG(1)**2-GG(2)**2                                           ALBEG 54
      BE1 = 0.5*WIK*CS                                                  ALBEG 55
      GA1 = 0.5*WIK*SN                                                  ALBEG 56
      EAL = ABS((AL-AL1)/AL)                                            ALBEG 57
      EBE = ABS((BE-BE1)/BE)                                            ALBEG 58
      EGA=0.0                                                           ALBEG 59
      IF(GA) 37,38                                                      ALBEG 60
   37 EGA=((GA-GA1/GA))                                                 ALBEG 61
   38 EE=AMAX1(EAL,EBE,EGA)                                             ALBEG 62
      IF(EE-1.0E-9) 40,40,99                                            ALBEG 63
   40 THETA(1) = THE*TORAD                                              ALBEG 64
      THETA(2) = THETA(1)+90.0                                          ALBEG 65
      XX = GG(1)-GG(2)                                                  ALBEG 66
      IF(XX) 43,42,42                                                   ALBEG 67
   42 RETURN                                                            ALBEG 68
   43 T = GG(1)                                                         ALBEG 69
      GG(1) = GG(2)                                                     ALBEG 70
      GG(2) = T                                                         ALBEG 71
      T = THETA(1)                                                      ALBEG 72
      THETA(1) = THETA(2)                                               ALBEG 73
      THETA(2) = T                                                      ALBEG 74
      RETURN                                                            ALBEG 75
   99 PRINT 199,G,R,N,S,AL,BE,GA,GG,THETA,AL1,BE1,GA1                   ALBEG 76
      RETURN                                                            ALBEG 77
      END                                                               ALBEG 78
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