AN ABSTRACT OF THE THESIS OF

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in Chemistry presented on March 3, 1978

Title: MAGNETIC PROPERTIES OF AN ANALOG COMPOUND FOR

CYTOCHROME P-450

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Abstract approved: H. Hollis Wickman

This thesis describes a Mossbauer effect and electron paramagnetic resonance study of iron (III) tetraphenylporphyrinatobenzenethiolate benzene thiol, an analog compound for bacterial cytochrome P-450. The compound is unusual in that it provides a model for the two ferric reaction states of cytochrome P-450. The iron in the model compound exhibits a gradual low spin to high spin transition over the temperature range 77 to 300 K.

Mossbauer spectra for several samples shows that the material, as prepared, consists of at least two species. At 4.2 K the Mossbauer pattern consists of a superposition of two low spin quadrupole doublets (\(\Delta E_1 = 0.282\) cm/sec, \(\delta_1 = 0.038\) cm/sec, \(\Delta E_2 = 0.175\) cm/sec, \(\delta_2 = 0.053\) cm/sec). The quadrupole splitting, \(\Delta E_1\), of the first component was broadened by paramagnetic hyperfine structure and has been described here by a model relaxation calculation. The EPR spectra at 4.2 K for the two low spin components were
similar and could not be resolved from data for polycrystalline samples. The \( g \) tensor at 4.2 K is 2.363, 2.240, 1.965. As temperature is increased both these low spin components interconvert to a high spin species with \( T_{c,1} \) near 120 K and \( T_{c,2} \) near 225 K. The Mossbauer and EPR data for the model compound are compared with similar data for the bacterial cytochrome P450 as reported by Gunsalas and co-workers. The data presented here are consistent with the results from other model compounds that contain sulfur as one of the axial ligands and which indicate probable sulfur ligation in the low spin ferric reaction state of cytochrome P450.
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Dean of Graduate School

Date thesis is presented ______March 3, 1918______

Typed by Deanna L. Cramer for Steven Wayne McCann
ACKNOWLEDGEMENTS

I would like to thank the following for their many contributions to my graduate career:

Hollis Wickman for suggesting this project, and for his guidance and advice. He was always there with a helpful suggestion when I needed it;

Robert Lytz, George Chapps, Fred Wells, James Grow and Ted Hopkins for their assistance in the lab and many helpful and friendly discussions;

John Archibald and Gerry Allison who kept the equipment working in spite of our best efforts, even when we needed it yesterday;

The National Science Foundation, the O.S.U. Computer Center and the O.S.U. Department of Chemistry for their financial assistance;

T. N. Sorrell and his thesis advisor J. P. Collman for giving us the opportunity to work on this project and for the initial samples;

W. E. Silverthorn for his time and effort in preparing the final samples used in this thesis;

My parents and the Freemans for their continued moral support and gentle prodding throughout my long graduate studies;

My wife, who has suffered many nights and long weekends alone while I pursued this elusive goal. Her unswerving support can never be adequately acknowledged.
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MAGNETIC PROPERTIES OF AN ANALOG COMPOUND FOR CYTOCHROME P-450

I. INTRODUCTION

Many important electron transport enzymes are conjugated proteins made up of a large number of amino acids and a metal containing prosthetic group, which is a non amino acid inorganic derivative. The metal ion environment in these enzymes often leads to interesting molecular magnetic and electronic properties. Because of preparative complications associated with native enzymes, inorganic analog compounds, consisting of the appropriate metal ion with ligation known or suspected to be that of the enzyme, are therefore of interest. These analog compounds are often easier to study than the enzyme, and they may potentially lead insight to the electronic and magnetic properties of the enzyme. This thesis deals with an analog complex for certain states of trivalent iron in the widely studied enzyme cytochrom P-450. Although this enzyme is of great biochemical importance, only a few analog complexes with ligation approximating that of cytochrome P-450 have been studied. Of these, the complex studied here is the only low spin ferric analog for which preliminary structural data are currently available.

The monooxygenase enzyme cytochrome P-450, commonly known as P450, is found in both mammalian and bacterial systems. P450 is a conjugated protein with protoporphyrin
IX (PPIX) as the prosthetic group. It differs from other known cytochromes and oxygen carrying heme proteins by exhibiting a Soret band at 450 nm for the ferrous carbonyl adduct. This gives the enzyme its name. In mammalian liver microsomes it plays a key role in the hydroxylation of such varied substrates as fatty acids, steroids, aniline, and a variety of drugs [1]. In the bacteria _Pseudomonas putida_, P450 is a soluble hydroxylase which transforms selected substrates, such as camphor, to a secondary alcohol [2].

While mammalian P450 has only recently been isolated with full retention of activity [3, 4, 5], the bacterial monooxygenase system is well known and the reaction cycle has been determined by Gunsalas, et al. [2], by observing the system _in vitro_ using highly purified components. At the start of the reaction cycle shown in Fig. 1, low spin ferric bacterial P450 (m°) is in the resting state. It binds a substrate, S, such as camphor, and the heme site is converted to a high spin ferric species (m°S). The resulting enzyme-substrate complex accepts an electron and is reduced to a high spin ferrous species (mRS). Molecular oxygen then binds to the ferrous species yielding a nonparamagnetic species (mRS02). Further reduction by the protein reductase (FAD) and redoxin (Pd) returns the P450 enzyme to its low spin ferric resting state and yields a hydroxylated substrate. This thesis is concerned with a model complex
Figure 1. Reaction cycle of cytochrome P450 in the bacteria Pseudomonas putida (from Ref. [2]).
for the high and low spin ferric states. Before describing the analog complex, it is useful to review the magnetic properties of the ferric ion in bacterial P450.

The low spin, $S = 1/2$ ferric state in P450 is characterized in solution by an electron spin resonance signal giving $g$ values at $g = 2.45, 2.26, 1.91$ [6], and a Mossbauer spectrum with $\Delta E_Q = 2.85$ mm/sec and $\delta = 0.38$ mm/sec [7]. When the solution is saturated with the substrate camphor, approximately 60-70% is converted to the high spin $S = 5/2$ substrate bound ferric state [8]. This state is characterized by an EPR spectrum with $g = 8, 4, 1.8$ and Mossbauer spectrum with $\Delta E_Q = 0.78$ mm/sec and $\delta = 0.44$ mm/sec [7]. The high spin substrate bound species is reduced by receiving an electron through the interaction of two proteins, reductase and redoxin, and yields a high spin, $S = 2$, ferrous ion with a Mossbauer spectrum of $\Delta E_Q = 2.45$ mm/sec and $\delta = 0.83$ mm/sec at 4.2 K [7]. This species then binds with molecular oxygen to yield a non-paramagnetic species with Mossbauer parameters at 4.2 K of $\Delta E_Q = 2.15$ mm/sec and $\delta = 0.31$ mm/sec, indicative of a low spin ferric system [7]. This species is probably a $\text{Fe}^{III} - \text{O}_2^-$ species similar to oxyhemoglobin [9]. We are returned to the starting point by the further action of the reductase and redoxin to yield the low spin ferric species and the hydroxylated camphor.

The exact nature of the local coordination sphere of the ferric P450 is the subject of recent literature. While
the equatorial coordination of the iron is well known to be a protoporphyrin IX ring, the exact nature of the axial ligation remains in question. In order to determine the nature of the axial ligands, several different models of the prosthetic group have been used for the equatorial group, and various axial ligands have been placed on these models and studied. Early work with protoporphyrin IX and other porphyrins used halides and amines for the axial ligation [10-13]. These studies showed the five coordinate species to be high spin ferric systems. More recently, work by Collman [14-17], Holm [18-21], and others [22, 23] has given strong evidence for a thiolate ion as an axial ligand. The possibility of an axial sulfur ligation was first suggested by Mason, et al. [24], and strengthened by the work of Bayer [25].

Collman, Holm, and their co-workers have shown a relationship between coordination and spin state in porphyrin complexes predicted by Hoard [26]. The low spin ferric models are six coordinate species while the five coordinate species are high spin. Work by Collman [14, 16] and Holm [21] has demonstrated that the exact nature of the sixth ligand has little effect on the EPR g values.

Our work is concerned with one of the six-coordinate model complexes originally prepared by Sorrell and Collman [14]. Iron (III) tetraphenylporphyrinatobenzenethiolate benzene thiol, Fe(TPP)(C₆H₅S)(C₆H₅SH) shows a temperature
dependent spin equilibrium between a low spin (LOW) and high spin (HIGH) states [27]. Structural and coordination changes accompany this spin equilibrium. Preliminary temperature dependent structural determinations by Strouse [15], shown in Fig. 2, show an equilibrium condition with both a five coordinate and six coordinate species present [72].

By using Mossbauer spectroscopy, electron spin resonance spectroscopy and magnetic susceptibility we have examined the temperature variation of this spin equilibrium. This thesis will examine the similarities and differences between the P450 enzyme system and the model complex. Because the model complex is more magnetically concentrated, relaxation rates are more rapid, leading to line broadening and motional narrowing. These effects, described here by a model calculation of Mossbauer lineshapes [28], limit our ability to compare accurately the magnetic hyperfine tensor for these cases. However, within the limits of the information available from these lineshape calculations, the results are similar to data reported for the P450 enzyme.
Figure 2. Five coordinate (top) and six coordinate forms of Fe(III) TPP(S\phi)(HS\phi) distances in angstroms (from Ref. [15]).
II. EXPERIMENTAL

A. Materials

The compound was supplied by T. N. Sorrell or locally prepared by W. E. Silverthorn according to the procedures by Sorrell and Collman [14]. Approximately 0.3 g of mesotetraphenylporphyrin iron (III) μ-oxo dimer was dissolved in 70 ml benzene and stirred for one hour with 75 ml of 15% $\text{H}_2\text{SO}_4$ and 10-15 ml of benzenethiol. The organic layer was separated and 75 ml of 95% ethanol added. The solution was evaporated slowly in a round bottomed flask under a stream of nitrogen to a volume of 20 to 50 ml. The solvent was decanted and the crystals washed with ethanol several times and dried under a stream of nitrogen. This yields approximately 0.2 g of Fe(TPP)(Sϕ)(HϕSϕ) which is an elongated deep purple crystal. The material is extremely soluble in benzene giving a dark brown solution.

The locally prepared materials were analyzed by Galbraith Laboratories and yielded the following:

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%Fe</th>
<th>%S</th>
</tr>
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<tr>
<td>SRL 12</td>
<td>76.00</td>
<td>4.40</td>
<td>6.34</td>
<td>6.34</td>
<td>6.99</td>
</tr>
<tr>
<td>SRL 14</td>
<td>75.49</td>
<td>4.47</td>
<td>6.38</td>
<td>6.40</td>
<td>7.00</td>
</tr>
<tr>
<td>Theory</td>
<td>75.76</td>
<td>4.40</td>
<td>6.31</td>
<td>6.30</td>
<td>7.23</td>
</tr>
</tbody>
</table>

Sorrell [15] reports that materials prepared in their laboratory also yielded excellent analysis.
B. Mossbauer Methodology

The Mossbauer spectrometer was of the conventional constant acceleration type [29, 30]. The source is $^{57}$Co diffused in rhodium [31]. All isomer shifts are given relative to natural iron foil at 300 K. The source was mounted on a LVsyn-loudspeaker system driven by a digitally controlled function generator with a standard feedback loop. The radiation was detected using a Reuter Stokes, nitrogen/methane proportional counter with low iron beryllium window, an Ortec 109 PC preamplifier, a Tennelec TC914 high voltage bias supply, a Tennelec TC205A linear amplifier, a Nuclear Data ND2400 multichannel analyzer with up-down multiscaling, a Nuclear Data Generation II 100 MHz analog to digital converter, and a Nuclear Data two-input zero dead time module. The output was obtained both visually on an oscilloscope and as paper tape on a teletype. For ease of use and storage the paper tape data was converted to card format and Calcomp plot using the OSU CDC 3300 computer. Details of the data analysis programs are given in Appendix I.

The sample holder used in the Mossbauer experiments was a two piece 2.22 cm diameter lucite disc with a sample thickness of 0.025 cm, sealed with silicon grease. The Lucite holder was sandwiched between two 0.025 cm low iron beryllium discs and fastened to an OFHC copper block. The copper block contained two 20 ohm heaters in parallel, a platinum resistance thermometer (PRT) and a silicon diode thermometer.
The sample was mounted in a Janis Research Company Model DT varitemp dewar, using liquid helium as a coolant for 4.2 K and below, and liquid nitrogen for the 77 K to 300 K range.

Sample temperature was controlled using a Lake Shore Cryotronics DTC-500 temperature controller connected to the silicon diode thermometer. The PRT was calibrated from 90 K to 273 K using the IPTS-68 temperature scale [32] and extended to 4.2 K using a Cragoe Z function [33]. The PRT was monitored using a 1.0 ma. constant current source and a digital voltmeter. For temperatures of 4.2 K and below, the temperature was controlled by pumping on liquid helium through a Lake Shore Cryotronics Model 329 vacuum regulator valve, and monitoring the vapor pressure.

C. Magnetic Susceptibility Apparatus

The susceptibility data was obtained by the Faraday method using a Cahn RG electrobalance and a Houston Instruments 2000 recorder. The magnetic field was provided by a six inch electromagnet and field gradient by a George Associates Model 503 Lewis Coil. The magnetic field was monitored using a Hall probe. A Janis Research Company Model DT helium research dewar was used for temperature control, employing the same methods as the Mossbauer experiments. The resistance of the PRT was corrected for the effect of the magnetic field, by obtaining readings both in
and out of the field at selected points and adjusting accordingly.

Samples of approximately 5 to 10 mg are encapsulated in aluminum foil to insure good thermal contact and placed in a quartz bucket which was suspended on a multifilament nylon thread in the sample insert (Fig. 3) located in the dewar. The distance from the balance to the sample was approximately 120 cm to insure isolation of the balance from the magnet and thermal isolation of the sample. The samples were easily changed through a side window, located near the balance.

D. Electron Paramagnetic Resonance Apparatus

The EPR measurements were obtained using a Varian E-9 spectrometer with an E-231 cavity operating in the TE\textsubscript{102} mode. Samples were mounted in standard 4 mm quartz EPR tubes. Temperatures from 300 K to 90 K were achieved using a stainless steel version of Jensen's [34] gas stream heat exchanger attached to a Scanco S-824 quartz dewar insert. Temperature was monitored with a PRT located in the gas flow between the heat exchanger and the sample, approximately 1.0 cm from the sample. Gas flow was kept at 10 l min\textsuperscript{-1} to ensure adequate cooling and minimize temperature gradients. Measurements made with another PRT replacing the sample indicated a gradient of less than 1 K over a 3 cm range.
Figure 3. Cross-sectional view of sample area of magnetic susceptibility apparatus.
The helium temperature EPR employed a different probe and dewar arrangement. The EPR probe was constructed locally and consists of a rectangular cavity operating in the $\text{TE}_{102}$ mode and a variable coupling slug as described by Gordon [35]. The probe was mounted in a Kontes Martin Helidewar and cooled with liquid helium. Samples were mounted in 2.5 mm quartz tubes and inserted from the bottom of the cavity.
III. THEORY

A. Introduction

The iron tetraphenylporphyrin complexes FeP-5 and FeP-6 studied in this thesis contain trivalent iron, denoted Fe$^{III}$, in a d$^5$ configuration. This configuration has a Hund's rule free ion ground state of $^6S$. When the ion is complexed with ligands, the energy levels of the free ion are perturbed in a way which is conveniently expressed by a Tanabe-Sugano diagram [36]. The level structure for the d$^5$ configuration in an octahedral ligand symmetry is given by Fig. 4 [37]. These levels may be further perturbed by lower symmetry ligand field components, spin orbit interactions and hyperfine interactions. The Hamiltonian which represents these perturbations is given by [38]

$$\mathcal{H} = \mathcal{H}_C + \mathcal{H}_{CF} + \mathcal{H}_{SO} + \mathcal{H}_{HE} + \mathcal{H}_Q + \mathcal{H}_{HN} + \mathcal{H}_{MHFS} \quad (1)$$

where

$$\mathcal{H}_C = \sum_k \left( \frac{p_k^2}{2m} - \frac{Ze^2}{r_k} \right) + \sum_{j<k} \frac{e^2}{r_{jk}} \quad (2)$$

is the Coulomb interaction of the electrons with the nucleus (assumed fixed) and with each other.

$$\mathcal{H}_{CF} = -e \sum_k V(\bar{r}_k) \quad (3)$$
Figure 4. Tanabe-Sugano diagram for $d^5$ electron configuration in an octahedral crystal field (from Ref. [37]). $\Delta$ is the crystal field strength, $B$ is interelectronic repulsion strength, and $E$ is the energy relative to the ground state energy.
is the interaction of the atomic electrons with the crystal field potential $V(\vec{r})$.

$$
\mathcal{H}_{SO} = \sum_k \zeta(r_k) \vec{r}_k \cdot \vec{s}_k \tag{4}
$$

is the interaction of the electron spins with the orbital motion of the electrons.

$$
\mathcal{H}_{HE} = \sum_k \frac{e\hbar}{2mc} (\vec{r}_k + 2\vec{s}_k) \cdot \vec{H}_o = \beta(\vec{r}_k + 2\vec{s}_k) \cdot \vec{H}_o \tag{5}
$$

is the interaction of the ion's electrons with an external magnetic field.

$$
\mathcal{H}_{MHFS} = 2g^n \beta_n \beta \sum_k \left\{ \frac{(\vec{r}_k + \vec{s}_k)}{r_k^3} + \frac{3(\vec{r}_k \cdot \vec{s}_k)(\vec{r}_k)}{r_k^3} \right\}
+ \frac{8\pi}{3} \delta(\vec{r}_k) \cdot \vec{s}_k \right\} \cdot \vec{I} \tag{6}
$$

is the interaction between the magnetic moment of the nucleus and the magnetic field set up by the orbital and spin moments of the electrons.

$$
\mathcal{H}_Q = \frac{eQ}{2I(2I-1)} (V_{zz}I_z^2 + V_{xx}I_x^2 + V_{yy}I_y^2) \tag{7}
$$

is the electrostatic interaction between the quadrupole moment of the nucleus and the electric field gradient at the nucleus [39].

$$
\mathcal{H}_{HN} = -g_n \beta_n \vec{H}_o \cdot \vec{I} \tag{8}
$$
is the interaction between the nucleus and an external magnetic field. The general forms of the operators are given here to show the full operator and will be discussed in subsequent sections.

The high spin state of Fe$^{III}$ occurs when the Coulomb term, $\mathcal{H}_C$, dominates the crystal field term in the Hamiltonian. The occupancy of the 5d orbitals leads to the free ion ground state $^6S$ which is six-fold degenerate in spin.

The actual ground state of Fe$^{III}$ is a many electron wavefunction. However, as is well known, the makeup of this state is conveniently represented by considering the occupancy of the one electron d orbitals in a ligand field. There are five d orbitals, denoted by $d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{z^2}$, $d_{x^2-y^2}$. In the absence of crystal fields, these orbitals are degenerate and are equally occupied by the 5 d electrons of Fe$^{III}$. All electrons have the spins parallel leading to the $S = 5/2$ ground state.

When the ion is placed in an octahedral ligand field, the five-fold orbital degeneracy is lifted, yielding two degenerate states labeled $e_g$ and three degenerate states labeled $t_{2g}$. The distribution of electrons in these two levels depends on the relative strength of the crystal field and Coulombic interactions. When $\mathcal{H}_{CF} >> \mathcal{H}_C$, a low spin, $S = 1/2$ ground state will result. When $\mathcal{H}_{CF} < \mathcal{H}_C$, a high spin, $S = 5/2$ state will result. For an intermediate case, $\mathcal{H}_C \sim \mathcal{H}_{CF}$, the ground state levels corresponding to these
configurations "cross over" each other as shown in Fig. 4. The high spin state \((t_{2g}^3 e_g^2)\) is labeled \(6A_1\), and the low spin state \((t_{2g}^5)\) is labeled \(2T_2\). The occupation of one-electron orbitals for the \(6A_1\) and \(2T_2\) states is shown as follows.

\[
\begin{array}{c}
\text{eg} & \uparrow & \uparrow \\
\text{t}_{2g} & \uparrow & \uparrow & \uparrow \\
\end{array}
\]

<table>
<thead>
<tr>
<th>high spin ((6A_1))</th>
<th>low spin ((2T_2))</th>
</tr>
</thead>
</table>

When the symmetry is less than octahedral, the crystal field is distorted, and part of the degeneracy of these states is lifted. In the case of FeP-5 and -6, the symmetry is \(C_{4v}\) which leaves the high spin state unchanged but causes the \(2T_2\) to split into a \(2B_2\) and \(2E\) states \([40]\). The \(2E\) state can be further split by spin-orbit interactions and higher order crystal field terms. By Kramers' theorem, however, a twofold degeneracy will always be present in the final level structure in the absence of a magnetic field.

These remarks show that octahedral metal complexes with the central ion in a \(d^4\), \(d^5\), \(d^6\), or \(d^7\) electronic configuration can exhibit one of two different electronic ground states \([41]\). In the case of a \(d^5\) configuration, either a \(2T_2\) or \(6A_1\) ground state can occur. When the coulombic repulsion term \((e^2/r_{jk})\) is of the same order as the crystal field splitting \((\mathbf{H}_{CF})\), a region, as seen in Fig. 4 at \(\Delta/B = 28\), exists where spin crossovers can occur. These cross-
overs can be of two types, a slow or gradual type and a fast or sudden type.

The more common type spin crossover is exhibited by the iron (III) tris-dithiocarbamates [42] where the reversible change from low spin to high spin form is a gradual function of temperature. The change takes place over a broad temperature range. This occurs when the energy separation $\Delta E$, of the low spin and high spin ground states, is of the order of $kT$. The transition from high spin to low spin is observed in the magnetic susceptibility data and is often accompanied by a decrease in metal ligand bond distances.

The second, less common type of spin crossover is illustrated by cis-dithiocyanatobis (1,10-phenanthroline) iron (II) [43] where a sharp reversible conversion between high spin and low spin forms occurs at a definite critical temperature without an accompanying structural phase transition. This is a first order phase transition and, in this example, is accompanied by a discontinuity in the heat capacity data, corresponding primarily to a sudden change in the magnetic susceptibility over a narrow temperature range.

B. Ground State Interactions

1) Low Spin Iron (III)

For the low spin iron (III) electronic states, it is assumed that the three $t_{2g}$ orbitals are low lying in energy and are widely separated from the $e_g$ orbitals and hence will
be the only d orbitals occupied. This results in the $^{2}T_{2}$ ground state term for Fe$^{III}$.

Since the $^{2}T_{2}$ state is the only state of interest, we need not be concerned with the octahedral crystal field Hamiltonian which separates the $t_{2g}$ and $e_{g}$ orbitals, but only the perturbation Hamiltonian which acts on the orbital components of $^{2}T_{2}$.

Instead of working with the complex five electron wave function represented by $^{2}T_{2}$, it is convenient to think of the configuration $t^5_{2g}$ as a hole in a complete $t^6_{2g}$ system [44]. The hole configuration is then isomorphous with the one electron orbitals commonly denoted $|XY>$, $|YZ>$, and $|XZ>$ which, in terms of spherical harmonics [45], are given by

$$
|XY> = \frac{1}{\sqrt{2}} \left( Y^2 \right)
$$

$$
|XZ> = \frac{1}{i\sqrt{2}} \left( Y^1 \right)
$$

$$
|YZ> = \frac{1}{\sqrt{2}} \left( Y^0 \right)
$$

or in terms of the orbital angular momentum states, denoted by $|\ell, \ell z>$

$$
|XY> = \frac{1}{\sqrt{2}} \left( |2,2> - |2,-2> \right) = |\zeta>
$$

$$
|XZ> = \frac{1}{i\sqrt{2}} \left( |2,1> - |2,-1> \right)
$$

$$
|YZ> = \frac{1}{\sqrt{2}} \left( |2,1> + |2,-1> \right)
$$
It is often convenient to work in a basis of near angular momentum eigenfunctions (dropping the \( l = 2 \) from our states for simplicity) given by

\[
|1\rangle = -\frac{1}{\sqrt{2}} (|YZ\rangle - i|XZ\rangle)
\]

\[
|-1\rangle = -\frac{1}{\sqrt{2}} (|YZ\rangle + i|XZ\rangle)
\]

\[
|\zeta\rangle = |XY\rangle
\]

The \( t^5_{2g} \) configuration is six fold degenerate (including spin). The hole in the otherwise full shell can reside in any of the six states. Hence the configuration given by \(|1\alpha\rangle\) would denote electrons in the \(|1\beta\rangle, |-1\alpha\rangle, |-1\beta\rangle, |\zeta\alpha\rangle\) and \(|\zeta\beta\rangle\) states, where \( \alpha \) and \( \beta \) are the usual designations for the spin states.

The axial and rhombic crystal field interactions and the spin orbit coupling are described by the spin Hamiltonian

\[
\mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{SO}} = D[\ell_z^2 - \ell(\ell+1)/3] + E[\ell_x^2 - \ell_y^2] - \lambda(\vec{\ell} \cdot \vec{s})
\]

\[
= D[\ell_z^2 - \ell(\ell+1)/3] + \frac{E}{2}[\ell_+^2 + \ell_-^2] - \lambda(\vec{\ell} \cdot \vec{s})
\]

We implicitly assume that the low symmetry crystal field axes coincide with the cubic crystal field axes. This would correspond in FeP-6 to having the tetraphenylporphyrin in the \( xy \) plane and the sulfurs along the \( z \) axis. Since these sulfurs are different from the pyrrol nitrogens, they will...
be the source of the axial distortion. The second term is a rhombic distortion of the crystal field. This term will differentiate between the x and y axes. The last term corresponds to the spin-orbit interaction.

The Hamiltonian matrix for this operator in the basis defined by Eq. (11) is

\[
\begin{pmatrix}
|1\alpha\rangle & |\zeta\beta\rangle & |-1\alpha\rangle & |-1\beta\rangle & -|\zeta\alpha\rangle & |1\beta\rangle \\
<1|\alpha & -D-\lambda/2 & -\lambda/\sqrt{2} & 3E & 0 & 0 & 0 \\
<\zeta|\beta & -\lambda/\sqrt{2} & 2D & 0 & 0 & 0 & 0 \\
<-1|\alpha & 3E & 0 & -D+\lambda/2 & 0 & 0 & 0 \\
<-1|\beta & 0 & 0 & 0 & -D-\lambda/2 & -\lambda/\sqrt{2} & 3E \\
-<\zeta|\alpha & 0 & 0 & 0 & -\lambda/\sqrt{2} & 2D & 0 \\
<1|\beta & 0 & 0 & 0 & 3E & 0 & -D+\lambda/2
\end{pmatrix}
\]

Upon diagonalization we find three Kramers doublets. The three pairs of eigenstates take the form

\[
|\psi_i^+\rangle = A_i |+1\alpha\rangle + B_i |\zeta\beta\rangle + C_i |-1\alpha\rangle \quad i=1,2,3
\]

and

\[
|\psi_i^-\rangle = A_i |-1\beta\rangle - B_i |\zeta\alpha\rangle + C_i |1\beta\rangle \quad i=1,2,3
\]

where A, B, and C are the coefficients of the diagonalized 3 x 3 submatrix and are real. This eigenvector can also be expressed in terms of the original basis (eq. (9)) as:

\[
|\psi_i^+\rangle = A_i^* |YZ>\alpha + B_i^* |XY>\beta + C_i^* |XZ>\alpha \quad i=1,2,3
\]

and

\[
|\psi_i^-\rangle = A_i^* |YZ>\beta - B_i^* |XY>\alpha - C_i^* |XZ>\beta \quad i=1,2,3
\]
where \( A' = -(A + C)/\sqrt{2} \)
\( B' = B \)
\( C' = i(A - C)/\sqrt{2} \)

The Zeeman interaction, expressed as an angular momentum operator by \( \beta \vec{H} \cdot (2\vec{s} + k\vec{\ell}) \), where \( k \) is the orbital reduction factor. The value of \( k \) is unity when there is no electron delocalization. When \( k \) is less than one, significant electron delocalization occurs. Theoretical work by Griffith has demonstrated that \( k \) can also have a value greater than one [46]. A value of \( k \) greater than unity stems from mixing of relatively low-lying excited states, resulting in an increase in the effective orbital angular momentum of the ground \( ^2T_2 \) term. When the above Zeeman Hamiltonian is equated to the same interaction in the spin formalism, the \( g \) values can be obtained directly.

\[
\hat{H}_z = \beta \vec{H} \cdot (2\vec{s} + k\vec{\ell}) = \beta \cdot \vec{H} \cdot \vec{g} \cdot \vec{S}_{\text{eff}} \quad (16)
\]

To use the spin formalism, we must assign the real eigenstate to some fictitious \( S = 1/2 \) spin state. Following the convention of Griffith [47] we assign

\[
| +\frac{1}{2} \rangle = | \psi^+ \rangle
\]

and

\[
| -\frac{1}{2} \rangle = | \psi^- \rangle \quad (17)
\]

so when we equate the corresponding matrix elements
\[
\begin{align*}
\langle \frac{1}{2} | \beta \ H_z \ g_z \ S_{\text{eff},z} | \frac{1}{2} \rangle &= \langle \psi^+ | \beta \ H_z (k \ l_z + 2S_z) | \psi^+ \rangle \quad (18)
\end{align*}
\]

we find

\[
(1/2)g_z = A^2 - B^2 + C^2 + k(A^2 - C^2)
\]

Summarizing, we have [47]

\[
\begin{align*}
g_x &= 2[2AC - B^2 + k\sqrt{2} (BC - AB)] \\
g_y &= 2[2AC + B^2 + k\sqrt{2} (BC + AB)] \\
g_z &= 2[A^2 - B^2 + C^2 + k(A^2 - C^2)]
\end{align*}
\quad (19)
\]

which, if \( k \) is unity, simplifies to [44]

\[
\begin{align*}
g_x &= 2(\sqrt{2}A + B)(\sqrt{2}C - B) \\
g_y &= 2(\sqrt{2}A + B)(\sqrt{2}C + B) \\
g_z &= 2(\sqrt{2}A + B)(\sqrt{2}A - B)
\end{align*}
\quad (20)
\]

2) High Spin Iron (III)

High spin iron (III) is observed when the \( t_{2g} \) and \( e_g \) levels are energetically close together and all five orbitals are populated. The resulting \( ^6A_1 \) ground state is perturbed in a complicated fashion by higher order crystal field and spin-orbit interactions which lead to a level structure which, in iron porphyrin, is approximated by the second rank crystal field spin Hamiltonian [48]:

\[
\mathcal{H}_{CF} = D(S_z^2 - S(S + 1)/3) + E(S_x^2 - S_y^2)
\quad (21)
\]
The first term is the axial crystal field distortion and the second term is the rhombic distortion. The basis wavefunctions are given by $|S,S_z>$. For $S = 5/2$, they are $|5/2, ±5/2>, |5/2, ±3/2>, \text{and } 5/2, ±1/2>$. The $6 \times 6$ matrix of this interaction, in block diagonal form, is (omitting the $S$ for simplicity)

$$
\begin{array}{cccccc}
|5/2> & |1/2> & |−3/2> & |−5/2> & |−1/2> & |3/2> \\
<5/2| & 10D/3 & 10E & 0 & 0 & 0 & 0 \\
<1/2| & 10E & −8D/3 & 3\sqrt{2}E & 0 & 0 & 0 \\
<−3/2| & 0 & 3\sqrt{2}E & −2D/3 & 0 & 0 & 0 \\
<−5/2| & 0 & 0 & 0 & 10D/3 & 10E & 0 \\
<−1/2| & 0 & 0 & 0 & 10E & −8D/3 & 3\sqrt{2}E \\
<3/2| & 0 & 0 & 0 & 0 & 3\sqrt{2}E & −2D/3 \\
\end{array}
$$

(22)

Diagonalization of this matrix yields three doubly degenerate eigenstates given by

$$
|\psi_i^±> = a_i |±5/2> + b_i |±1/2> + c_i |±3/2> \quad i=1,2,3
$$

(23)

The form of the $g$ values, $g_x$, $g_y$, and $g_z$ has been explicitly determined by Wickman, et al. [48]. For each level, they are given by

$$
g_{x,i} = g_J(3b_i^2 + 2\sqrt{5}a_i c_i + 4\sqrt{2}b_i c_i)
$$

$$
g_{y,i} = (-1)^{i+1} g_J(3b_i^2 + 2\sqrt{5}a_i c_i - 4\sqrt{2}b_i c_i)
$$

(24)

$$
g_{z,i} = (-1)^{i+1} 2g_J(5/2 a_i^2 + 1/2 b_i^2 - 3/2 c_i^2)
$$
when \( g_J = 2 \) and \( i = 1,2,3 \).

The problem can be simplified if we define one parameter \( \lambda = E/D \), for then the coefficients \( a_i, b_i, c_i \) of the wavefunction depend only on the parameter \( \lambda \). All physically distinct cases can be represented by a value of \( \lambda \leq 1/3 \), and the order of the states determined by the sign of \( D \) [49].

**C. Hyperfine Interactions**

Hyperfine interactions describe the coupling of the nucleus with its surrounding and was denoted \( \mathcal{H}_{\text{MHFS}} + \mathcal{H}_Q \) in Eq. (1). The total hyperfine Hamiltonian is given by

\[
\mathcal{H} = \frac{e^2}{2I(2I-1)} \left( V_{zz} I_z^2 + V_{xx} I_x^2 + V_{yy} I_y^2 \right) - g_n B_n \vec{I} \cdot \vec{H} \tag{25}
\]

where the first term is the electric quadrupole interaction, and the second term is the magnetic hyperfine interaction, with \( \vec{H} \) representing electronic operators discussed below. Both of these terms are small perturbations on the overall splitting of the ground and excited nuclear levels, yielding the separate lines observable in the Mossbauer spectra.

The parameters in the quadrupole Hamiltonian are: \( e \), the charge on the electron; \( Q \), the nuclear quadrupole moment; \( I \), the nuclear spin, \( I_j \), the projection of the nuclear spin on the \( j \) axis; and \( V_{jj}, \partial^2 V/\partial j^2 \), the \( j \)th component of the electric field gradient (EFG). The electric field gradient is a symmetric \( 3 \times 3 \) second rank tensor and is
made diagonal by the appropriate choice of axis system called the principal axis system. Further, since Laplace's equation must be obeyed, the tensor is traceless, thus

\[ V_{xx} + V_{yy} + V_{zz} = 0. \]  

(26)

Therefore, the electric field gradient can be specified by only two independent parameters. Conventionally these parameters are:

\[ eq = V_{zz} \]

and

\[ \eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \]  

We can rewrite the quadrupole portion of the equation above, using the new parameters, for Fe\(^{57}\)

\[ \mathcal{H}_Q = \frac{e^2 q_0}{12} \left[ 3I_z^2 - \frac{15}{4} + \eta(I_x^2 - I_y^2) \right] \]

or

\[ \mathcal{H}_Q = \frac{e^2 q_0}{4} \left[ I_z^2 - 5/4 + \eta/6(I_+^2 + I_-^2) \right] \]  

(28)

The ground nuclear state, \( I = 1/2 \), of Fe\(^{57}\) is not split by this Hamiltonian, since \( Q = 0 \). Diagonalization of the Hamiltonian matrix in the principal axis system for the different \( I_z \) levels of the \( I = 3/2 \) first excited state yields, by Kramers Theorem, two two-fold degenerate eigenstates separated in energy by
The electric field gradient arises from two sources. (1) The non-cubic valence electron distribution on the Fe ion. Since the inner filled molecular orbitals have spherical symmetry, they will not contribute to the EFG. This contribution will have a temperature dependence based on a Boltzmann distribution over low lying empty orbitals. (2) The non-cubic distribution of charges in the lattice about the iron site.

These terms are modified by the Sternheimer shielding factors which account for distortions of the ion core by the EFG. The effect of these factors tends to reduce the contribution from valence electrons and enhances the contribution from the more distant lattice terms. Mathematically, the above is given by

\[ q = (1 - R)q_{\text{val}} + (1 - \gamma)q_{\text{latt}} = V_{zz}/e \]  

\[ \eta q = (1 - R)\eta q_{\text{val}} + (1 - \gamma)\eta q_{\text{latt}} = (V_{xx} - V_{yy})/e \]  

where \( q_{\text{val}} \) and \( q_{\text{latt}} \) are the valence and lattice contribution to the EFG and \( (1 - R) \) and \( (1 - \gamma) \) are the Sternheimer shielding terms.

Since we know the form of the electronic wavefunction for the low spin ferric case, the valence contribution to the EFG can be calculated directly. To do this, matrix
elements of the forms

\[ \langle \psi_i^+ | \hat{q}_{\text{val}} | \psi_i^+ \rangle \quad \text{and} \quad \langle \psi_i^+ | \eta \hat{q}_{\text{val}} | \psi_i^+ \rangle \]

need to be evaluated. The relevant Hamiltonians are given by [50]

\[
\hat{q}_{\text{val}} = \frac{V_{zz}}{e} = \frac{3z^2 - r^2}{r^2} = \frac{16\pi}{5} \left( \frac{1}{5} \right)^{1/2} \frac{Y^0_2}{r^3} <r^{-3}> \quad (32)
\]

and

\[
\eta \hat{q}_{\text{val}} = \frac{V_{xx} - V_{yy}}{e} = \frac{3x^2 - y^2}{2r^5} = \frac{3}{2} \frac{32\pi}{15} \left( \frac{1}{5} \right)^{1/2} <r^{-3}> \left[ Y^2_2 + Y^{-2}_2 \right] \quad (33)
\]

At this point it should be noted that we have been using only atomic orbitals for the calculations for the low spin ferric problem. For calculations of the electron-nuclear interactions, it is better to use molecular orbitals, which are linear combinations of atomic orbitals that have the symmetry of the complex. It is convenient to do the electronic calculation as a crystal field calculation on atomic orbitals, then include covalency in the form of a proportionality constant. This assumes only that the symmetry of the original $t_{2g}$ orbitals is the same as the final molecular orbital wavefunctions. We will therefore rewrite the wavefunctions, including the covalency scaling factor, in terms of the more geometric basis $|XY>, |XZ>, |YZ>$
\[ |\psi^+\rangle = C_1 |XY\rangle + C_2 |XZ\rangle + C_3 |YZ\rangle \] (34)

where

\[ C_1 = BN_{xy} \]
\[ C_2 = \frac{i}{2} (A - C) N_{xz} \]
\[ C_3 = -\frac{1}{2} (A + C) N_{yz} \]

and

\[ N_{xy}, N_{xz}, N_{yz} \] are the covalency factors for the respective atomic wavefunction.

Evaluating the appropriate matrix elements we find that

\[ <\psi^+ | \hat{q}_{\text{val}} | \psi^+ > = \frac{2}{7} <r^{-3} > \left[ \frac{1}{2} (A^2 + C^2) (N_{xz}^2 + N_{yz}^2) - 2B^2 (N_{xy}^2) \right. \]
\[ + \left. AC(N_{yz}^2 - N_{xz}^2) \right] \] (35)

and

\[ <\psi^+ | \hat{n}_{\text{q}_{\text{val}}} | \psi^+ > = \frac{6}{7} <r^{-3} > \left[ \frac{1}{2} (A^2 + C^2) (N_{xz}^2 - N_{yz}^2) - AC(N_{yz}^2 + N_{xz}^2) \right] \] (36)

rearranging gives

\[ \eta = \frac{n_{\text{q}_{\text{val}}}}{q_{\text{val}}} = \]
\[ \frac{3 \left[ \frac{1}{2} (A^2 + C^2) (N_{xz}^2 - N_{yz}^2) - AC(N_{yz}^2 + N_{xz}^2) \right] \] (37)
\[ \left[ \frac{1}{2} (A^2 + C^2) (N_{xz}^2 + N_{yz}^2) - 2B^2 (N_{xy}^2) + AC(N_{yz}^2 - N_{xz}^2) \right] \]

However, these matrix elements only give the contribution to the EFG from one of the eigenstates. To find \( q_{\text{val}} \)
and $n_{\text{val}}$ we must take the Boltzmann sum of all available states. Assuming a fast electronic relaxation over these levels, we have the usual result [50]

$$q_{\text{val}} = \frac{\sum_{i=1,3} <\psi_i^+|q_{\text{val}}^i|\psi_i^+> e^{-(E_i - E_1)/kT}}{\sum_{i=1,3} <\psi_i^+|\psi_i^+> e^{-(E_i - E_1)/kT}}$$  \hspace{1cm} (38)$$

and

$$\eta q_{\text{val}} = \frac{\sum_{i=1,3} <\psi_i^+|\eta q_{\text{val}}^i|\psi_i^+> e^{-(E_i - E_1)/kT}}{\sum_{i=1,3} <\psi_i^+|\psi_i^+> e^{-(E_i - E_1)/kT}}$$  \hspace{1cm} (39)$$

where $|\psi_i^+>$ and $E_i$ are the eigenvectors and energies for the electronic wavefunctions in Eq. (34).

The lattice contribution to the quadrupole interaction is obtained by taking a sum over all charges in the crystal lattice. This interaction is usually small and has not played an important role in studies of biological samples and biological model complexes.

Since the $^{57}$Fe nucleus has a magnetic moment for both the ground and excited states, the presence of a magnetic field will split these states according to

$$\mathbf{H}_{\text{MHFS}} = -g_n \beta_n \mathbf{I} \cdot \mathbf{H}$$  \hspace{1cm} (40)$$

where $g_n$ is the nuclear gyromagnetic ratio ($g_n = 0.1806$, $-0.1033$ for the ground and first excited states
respectively) and $\beta_n$ is the nuclear magneton. For molecules with the iron as a paramagnetic center, the unpaired electrons near the nucleus will give rise to various terms in the hyperfine Hamiltonian. The Hamiltonian for an $n$ electron system can be written \[ H_{\text{MHFS}} = \mathcal{P}(\vec{L} \cdot \vec{I} - \kappa \vec{S} \cdot \vec{I} + \frac{1}{7} \sum_{k=1}^{n} \vec{a}_k \cdot \vec{I}) - g_n \beta_n \vec{I} \cdot \vec{H}_{\text{ext}} \] (41)

where

$$\vec{a}_k = 4\vec{s}_k - (\vec{l}_k \cdot \vec{s}_k)\vec{l}_k - \vec{s}_k(\vec{l}_k \cdot \vec{s}_k)$$
(42)

and

$$\mathcal{P} = 2g_n \beta_n \beta <r^{-3}>_{\text{eff}}$$
(43)

In these equations: $\beta$ = electron magneton; $\vec{L}$ is the total angular momentum which is a vector sum of the angular momentum, $\vec{l}_k$ for all the $k$ electrons; $\vec{S}$ is the total spin, and also a vector sum over the individual electron spins $\vec{s}_k$. The first term in the Hamiltonian arises from the interaction of the electron motion with the nucleus where the electrons are regarded as current loops. For high spin iron (III), $L = 0$, and hence this term does not contribute. The second term, involving $\kappa$, is the Fermi contact interaction resulting from the direct coupling between the nucleus and an s-electron. This coupling is actually two effects: first, the polarization of the core s electrons by exchange effects with unpaired 3d electrons; and second,
a small amount of 4s electron character in the 3d electrons. The third term is due to dipole--dipole interactions of the electrons with the nucleus. This term will also be zero for the high spin ferric case. The final term is the interaction of the nuclear moment with an externally applied field.

The Fermi contact constant, $\kappa$, is analogous [7] to the $k$ term used in calculating the $g$ tensor. The $<r^{-3}>_{\text{eff}}$ is the effective value of the radius of the 3d levels. It is proportional to a shielding factor analogous to the Sternheimer shielding factor. The effective field at the nucleus per unit spin, given by $P\kappa/g_n\beta_n$, is commonly quoted and has a value ranging from 190 kilogauss to 220 kilogauss for a large range of ferric and ferrous compounds [51, 52].

For convenience, we will rewrite the magnetic hyperfine Hamiltonian using the effective spin formalism.

$$\mathcal{H}_{\text{MHFS}} = \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{\hat{S}}$$

By equating matrix elements of this Hamiltonian with that of Eq. (41) we can find the hyperfine tensor $A$ for the low spin ferric case in terms of the coefficients of the appropriate wavefunctions, $P$ and $\kappa$. Using table A-41 of Griffith [47] to help evaluate Eq. (42), and the wavefunction of Eq. (14) we find [53]
\[ A_x = P \left[ 2\sqrt{2}B(C-A) - \kappa(2AC-B^2) - \frac{1}{7}(2B^2+6C^2-3\sqrt{2}AB+2AC-3\sqrt{2}BC) \right] \]

\[ A_y = P \left[ 2\sqrt{2}B(C+A) - \kappa(2AC+B^2) - \frac{1}{7}(-2B^2-6C^2+3\sqrt{2}AB+2AC-3\sqrt{2}BC) \right] \]

\[ A_z = P \left[ 2(A^2-C^2) - \kappa(A^2-B^2+C^2) + \frac{2}{7}(1+B^2-3\sqrt{2}AB) \right] \]

If the covalency factors \( N_{xy}, N_{yz}, \) and \( N_{xz} \) are included and the wavefunctions of Eq. (34) are used, we find:

\[ A_x = \frac{P}{2} \left[ 8C_1C_2i-2\kappa(-C_1^2+C_2^2+C_3^2)+\frac{2}{7}(-2C_1^2+2C_2^2-4C_3^2-6C_1C_3+6iC_2C_3) \right] \]

\[ A_y = \frac{P}{2} \left[ -8C_1C_3-2\kappa(C_1^2+C_2^2+C_3^2)+\frac{2}{7}(2C_1^2-4C_2^2+2C_3^2+6C_1C_3-6iC_2C_3) \right] \]

\[ A_z = P \left[ 4C_2C_3i+\kappa(C_1^2+C_2^2-C_3^2)-\frac{2}{7}(-2C_1^2+C_2^2-C_3^2-3iC_1C_2-3C_1C_3) \right] \]

which reduce to Eq. (45) if \( N_{xy} = N_{xz} = N_{yz} = 1. \)

For the high spin ferric case (orbital singlet), the valence contribution to the EFG and the anisotropic (orbital and dipolar) portions of the magnetic hyperfine interaction vanish. Then Eq. (25) would be simplified to

\[ \mathcal{H} = \mathcal{H}_{\text{MHS}} = A \cdot \mathbf{i} \cdot \langle S \rangle_{\text{eff}} + g_n \beta_n \mathbf{i} \cdot \mathbf{H}_{\text{ext}} \]

where \( \langle S \rangle_{\text{eff}} \) is the effective spin. However, lattice contributions to the EFG and higher order crystal field and spin orbit interactions give rise to admixtures to the \( ^6A_1 \) ground state which yield small anisotropic contributions to the total EFG and magnetic hyperfine interaction tensor \( A \). The interaction of this EFG and hyperfine tensor with the nucleus is governed by the same Hamiltonian as for the low
spin case, Eqs. (28) and (44). In practice, however, direct calculation of the hyperfine parameters and the EFG are generally not feasible in the high spin case.

D. Relaxation Theory

Recent literature has discussed the relative merits of two different theories used to calculate the effects of electronic relaxation on Mossbauer spectra for the $S = 1/2$ case. One theory, by Clauser and Blume [54], is a stochastic treatment of the problem, while Hirst [55] uses a perturbation treatment. We use Hirst's theory, as expanded by Hartmann-Boutron and Spanjaard [56] and applied by Shenoy and Dunlap [28]. The theory summarized here follows Shenoy and Dunlap and references therein.

In the presence of relaxation effects, the expression for the Mossbauer lineshape is given by

$$\mathcal{I}(\omega) = \text{Re}[F(p)]$$

(48)

where

$$F(p) =$$

$$\sum_{\text{all indices}} \left< \mu n | M_{LM}^{+} | \nu m \right> \left< \mu n \nu m \right| \bar{U} \left| \mu' n' \nu' m' \right> \left< \nu' m' | M_{LM}^{-} | \mu' n' \right>$$

(49)

$M_{LM}$ is an electromagnetic multipole operator of multipolarity $L$ and polarization $M$ which induces transitions between various hyperfine levels.
The superoperator $\tilde{U}$ contains the physical information about the system and is defined by the total Hamiltonian $H_0$, for the electron-nuclear system. Its matrix elements can be defined by the quantum mechanical time average of the evolution operator

$$\exp\left[\int_0^t H_0(t') dt'\right] = \tilde{\Gamma}(t)$$

(50)

$$\langle \mu n | \tilde{\Gamma}(t) | \mu'n'\rangle \langle \nu m | \tilde{\Gamma}^+(t) | \nu'm'\rangle_{\text{ave}} \equiv \langle \mu n \nu m | \tilde{U} | \mu'n' \nu m \rangle$$

Because of the separate time ordered series in (50), its evaluation is somewhat complex. As shown by Blume [51], for example, the averaging process leads to the formal introduction of the operator $\tilde{U}$ which is readily defined in various approximations and which satisfies

$$\tilde{U} = U^{-1} \equiv [p\tilde{\Gamma} - \frac{i}{\hbar} H^X_0 - R]^{-1}$$

(51)

with $p = \Gamma - i\omega$, $\Gamma$ the natural linewidth of the resonance line, $H^X_0$ the Liouville operator involving the static hyperfine interactions and $R$ a matrix containing information on the coupling of the various transitions due to the relaxation processes and involving the interaction between the ion and the bath. $|\mu n \nu m\rangle$ is the basis set of wavefunctions.

A Liouville operator is an operator which operates on other operators. If we have a quantum mechanical operator $A$ with an associated Liouville operator $A^X$, the operator $A^X$ will act on other quantum mechanical operators $B$ such that
\( A^X B \) gives the commutator of \( A \) and \( B \).

\[
A^X B = [A,B] = AB - BA
\]  

(52)

The physical significance of these operators for a Hamiltonian \( \mathcal{H}^X \) is found when seeking its eigenvalues and eigenvectors. If \( |\mu> \) and \( |\nu> \) are eigenvectors of the Hamiltonian \( \mathcal{H} \) associated with the Liouville operator \( \mathcal{H}^X \) and we have

\[
\mathcal{H} |\nu> = E_\nu |\nu>
\]  

(53)

and

\[
\mathcal{H} |\mu> = E_\mu |\mu>
\]

Then \( |\mu><\nu| \) can be thought of as a transition operator, which is an eigenoperator of \( \mathcal{H}^X \), such that [57]

\[
\mathcal{H}^X |\mu><\nu| = \mathcal{H} |\mu><\nu| - |\mu><\nu| \mathcal{H} = (E_\mu - E_\nu) |\mu><\nu|
\]

(54)

Thus the eigenvalues for the operator \( \mathcal{H}^X \) are the energy differences \( E_\mu - E_\nu \) of the energy levels of the eigenfunctions of \( \mathcal{H} \). These differences are the positions of the physically observed spectral lines.

Further, the matrix elements of an ordinary operator \( A \) can be used to define the matrix elements of the Liouville operator \( A^X \)

\[
<\nu|A^X|\mu'> = \delta_{\nu\nu'} <\mu|A|\mu'> - \delta_{\mu\mu'} <\nu'|A|\nu'>
\]

(55)

These properties of the Liouville operator are used in solving the relaxation problem.
Since we wish to consider all possible transitions and how they are coupled to all others, we need a basis which contains all possible nuclear and electronic states. A vector consisting of the $z$-component of the nuclear ground state spin $I^g_z$, the electronic spin $S^e_z$ when the nucleus is in the ground state, and the corresponding spins in the excited state $I^e_z$ and $S^e_z$. Thus, the basis vector is given by $|\mu \nu \nu m\rangle = |S^g_z I^g_z S^e_z I^e_z\rangle$.

Let us now examine each term of Eq. (49). The terms involving $M^M_{LM}$ and $M^M_{LM}$ are matrix elements of the electromagnetic multipole operator which gives the probability amplitude for a transition from nuclear state $m$ to $n$ with multipolarity $L$ and polarization $M$ where $M = m - n$. These are given by

$$<\nu'\mu' | M^M_{LM} | \mu \nu n'> = \delta_{\nu \mu'} \delta_{\nu \mu} C_{\mu \nu}'^{LM}$$

and

$$<\mu n | M^M_{LM} | \nu m> = \delta_{\mu \nu} (C^{LM}_{nm})^+$$

where $C^{LM}_{mn}$ are basically transition probabilities. These are tabulated in table 1 for powder samples for $I^g = 1/2$ to $I^e = 3/2$ transitions for magnetic dipole ($M1, L = 1$) and electric quadrupole ($E2, L = 2$) cases. As shown, for example by Blume [57] or Gabriel [58], Eq. (49) reduces to

$$F(p) = \sum_{\text{all indices}} (C^{LM})^+ (C^{LM}_{mn}) <\mu \nu \nu m | | u^{-1} | u' n' \nu' m'>$$

(57)
Table 1. Transition probability amplitudes $C_{nm}^{LM}$ for nuclear spins $I^g = 1/2$ and $I^e = 3/2$ with $M_1$ and $E2$ character (from Ref. 59).

<table>
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<tr>
<th>$n$</th>
<th>$m$</th>
<th>$M$</th>
<th>$L=1$</th>
<th>$L=2$</th>
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<td>$\sqrt{1/20}$</td>
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</tr>
<tr>
<td>-1/2</td>
<td>3/2</td>
<td>2</td>
<td>0</td>
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</tr>
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<td>0</td>
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<tr>
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<td>-3/2</td>
<td>-1</td>
<td>$\sqrt{3/12}$</td>
<td>$\sqrt{1/20}$</td>
</tr>
</tbody>
</table>
In matrix notation, this becomes

\[ F(p) = \sum_{LM} (C_{LM})^+ \ U^{-1} \ (C_{LM}) \]  

(58)

where only elements of \( U^{-1} \) with \( \nu' = \mu' \) and \( \nu = \mu \) will contribute (from Eq. (56)).

The Liouville operator \( \mathcal{H}_0^X \) in \( \tilde{U} \) involves the static (non-relaxation) hyperfine interactions. The matrix elements for this operator are based on the Hamiltonian

\[ \mathcal{H}_0 = \mathcal{H}_Q + \mathcal{H}_{\text{MHFS}} \]  

(59)

and have matrix elements of the form

\[ \langle \nu \nu' \mu | \mathcal{H}_0^X | \mu' \nu' \mu' \rangle = \delta_{\nu \nu'} \delta_{\mu \mu'} \langle \nu \nu' | \mathcal{H}_{\text{MHFS}} | \mu' \nu' \rangle - \delta_{\mu \mu'} \delta_{\nu \nu'} \langle \nu' \mu | \mathcal{H}_Q^* + \mathcal{H}_{\text{MHFS}}^* | \nu \mu' \rangle \]  

(60)

where \( \mathcal{H}_{\text{MHFS}} \) is the magnetic hyperfine interaction given in Eq. (44) for \( A \) being the ground state magnetic hyperfine tensor and \( \mathcal{H}_{\text{MHFS}}^* \) is the same interaction with the excited state magnetic hyperfine tensor where

\[ \tilde{A}/g_n = \tilde{A}^*/g_n^* \]  

(61)

Since \( \mathcal{H}_Q \) is zero for the ground state, it does not contribute to \( \mathcal{H}_o \) but does contribute to the excited state term.

The matrix \( R \) contains all relevant information concerning the couplings of the various transitions. It is assumed that the interaction can be described as a coupling
of the spin $S$ to an average time-dependent field $\mathbf{H}(t)$ set up by the bath

$$\mathbf{H} = \mathbf{S} \cdot \mathbf{\alpha} \cdot \mathbf{H}(t)$$  \hspace{1cm} (62)

If the interaction is assumed to be a true magnetic type, as in the common spin-spin interaction, then $\mathbf{\alpha} = \mathbf{\tilde{g}} \mathbf{\beta}$ where $\mathbf{\tilde{g}}$ is the gyromagnetic $g$ tensor of Eq. (19). The relaxation operator $\hat{\mathbf{R}}$ then depends only on the spectral density $J_q(\omega)$ which is a linear combination of Fourier transforms of the time averaged correlation functions for the field $\mathbf{H}(t)$. If it is assumed that $J_q(\omega) = J_q(0) \equiv J_q$ and that $\mathbf{H}(t)$ is isotropic, then a relaxation rate $W_i$, $(i = x, y, z)$ can be defined.

$$W_i = \frac{1}{2} g_i^2 \beta^2 J_q$$  \hspace{1cm} (63)

In terms of this relaxation rate, the relaxation matrix is given by

$$<\mu \nu m | \hat{\mathbf{R}} | \mu' n' \nu' m'>$$

$$= \delta_{nn'} \delta_{mm'} \{ \delta_{\mu \mu'} \delta_{\nu \nu'} [W_z (2 <\nu | S_z | \nu' > <\mu' | S_z | \mu > - \frac{1}{2}) - \frac{1}{2} (W_x + W_y)] \\
+ \left[ \frac{1}{2} (W_x + W_y) \right] [<\nu | S_+ | \nu' > <\mu' | S_+ | \mu > + <\nu | S_- | \nu' > <\mu' | S_- | \mu > ] \\
+ \left[ \frac{1}{2} (W_x - W_y) \right] [<\nu | S_+ | \nu' > <\mu' | S_+ | \mu > - <\nu | S_- | \nu' > <\mu' | S_- | \mu > ] \}$$  \hspace{1cm} (64)

Using the above and a procedure suggested by Clauser [60], the Mossbauer spectra can now be calculated. By obtaining the eigenvalues $\lambda$ and the eigenvectors $\mathbf{V}$ of $\mathbf{U}$ for
the case \( \omega = 0 \), then (49) can be re-expressed as

\[
F(p) = \sum_{m} (M_{LM}^+ \cdot \bar{\nu})(\bar{\lambda} - i\omega \bar{\lambda})^{-1} (\bar{\nu}^{-1} \cdot M_{LM})
\]  \( (65) \)

E. Effect of Small External Magnetic Fields

The foregoing discussion is sufficient to describe an electron nuclear level structure and the resulting Mossbauer hyperfine structure, including relaxation effects. Depending upon energy differences between hyperfine structure levels and electronic relaxation rates, \( \tilde{W}_i \), complex or ill-resolved spectra may occur (Section D).

In zero field, spin relaxation occurs between levels which are admixtures of \( m_S \) and \( m_I \) states. Paramagnetic fields equivalent to 200 kOe may be present. Electronic transition rates, among these complex, unequally spaced level structures may be "slow" \( (\Omega_S \sim \Omega_L = g_n \beta_n H_{\text{int}/\hbar}) \) and lead to ill-resolved hyperfine structure. However, if a polarizing field of sufficient strength \( (H_{\text{ext}} > 15 \text{ G}) \) is applied so that the electron Zeeman interaction dominates the electron nuclear hyperfine coupling, the situation changes. Now the spins are polarized and \( m_S \) is a good quantum number. Because of the small polarization of the \( <S> \) ion, the size of \( H_{\text{int}} \) is now reduced, so that \( \Omega_S > \Omega_L \) and the nuclear hyperfine structure consists of a quadrupole interaction and a small electron-nuclear Zeeman interaction.
The result is a well resolved quadrupole doublet which considerably simplifies interpretation of the Mossbauer hyperfine structure pattern.
IV. CALCULATIONS

The calculations in this thesis are divided into four parts. First, we obtain $g$-values from the EPR data and from these we obtain the ground state wavefunctions, and the crystal field parameters. Second, using the crystal field parameters and additional constants, calculate the wavefunctions for the three $S = 1/2$ doublets and obtain the theoretical $g$-tensor, the hyperfine $A$ tensor, and the valence contribution to the EFG. Third, using parameters from the second step, calculate out the Mossbauer spectra from the $g$ values, hyperfine tensor, EFG, and relaxation information. Fourth, calculate a theoretical $S = 1/2$ EPR spectrum, which brings us back to the starting point of the calculations.

To calculate the ground state wavefunctions and crystal field parameters, we will make use of Eqs. (13), (14), (19) and (20), which will be repeated for convenience. Using the wavefunctions of Eq. (14) and replacing $\alpha$ and $\beta$ with $+$ and $-$ to denote spin, we have

$$|\psi_1^+> = A_1 |\pm 1^+> \pm B_1 |\xi^+> + C_1 |\mp 1^{-}>$$  \hspace{1cm} (14)

where, when $k$ is unity, has $g$ values
If we assume $k$ is unity, it can be shown that [61]

\[
A = \frac{(2g_x + g_y - g_z)}{4(g_z + g_y - g_x)}^{1/2}
\]

\[
B = \frac{(g_y - g_x)}{2(2(g_z + g_y - g_x))}^{1/2}
\]

\[
C = \frac{(g_y + g_x)}{4(g_z + g_y - g_x)}^{1/2}
\]

Using this in the normalizing condition on the wavefunction $A^2 + B^2 + C^2 = 1$ gives us [62]

\[
\frac{g_x^2 + g_y^2 + g_z^2 + g_y g_z - g_x g_y - g_x g_z}{4(g_y + g_z + g_x)} = 1
\]

Since the EPR spectrum only gives us the modulus of the $g$ values and no information about ordering them, all 48 possible permutations of signs and axis assignments must be tried. We find that 24 combinations lead to an imaginary wavefunction (left hand side of Eq. (67) is negative) and are therefore discarded. The remaining 24 combinations can be divided up into four groups of six which leave the normalization condition (LHS of Eq. (67)) invariant under six permutation operations.

The wavefunction coefficients from Eq. (66) for the remaining permutations are normalized to unity and these
values are used as initial estimates to fit the experimental g values to the equations

\[ g_x = 2[2AC - B^2 + k\sqrt{2} (BC - AB)] \]
\[ g_y = 2[2AC + B^2 + k\sqrt{2} (BC + AB)] \]
\[ g_z = 2[A^2 - B^2 + C^2 + k(A^2 - C^2)] \]  
(19)

The parameters are fit to the experimental results based on a four dimensional Newton's method approach.

In general, the n-dimensional Newton's method is used to solve a system of n equations, given in vector notation as

\[ \vec{f}(\vec{x}) = \vec{0} \]  
(68)

If we have a starting vector \( \vec{a} \), then we can expand the function about \( \vec{a} \), retaining only the linear terms of the Taylor series expansion in n space. By setting these equations equal to zero, we have [63]

\[ 0 = \vec{f}(\vec{a}) + (\nabla f) \cdot \Delta \]  
(69)

After solving this set of equations for the vector \( \Delta \), the new approximation to the solution is given by

\[ \vec{b} = \vec{a} + \Delta \]  
(70)

This is continued until either the method has converged to give a very small \( \Delta \) or, after a set number of attempts, the
convergence criteria is not met, at which time a new initial guess has to be tried.

For our case, let us denote the experimental set of \( g \) values based on the permutation of signs and axes by \( g_x', g_y', \) and \( g_z' \). The equations we are trying to solve are given by

\[
\begin{align*}
0 &= g_x(A, B, C, k) - g_x' \\
0 &= g_y(A, B, C, k) - g_y' \\
0 &= g_z(A, B, C, k) - g_z \\
0 &= A^2 + B^2 + C^2 - 1
\end{align*}
\]

Armed with our initial estimates \( A, B, C, \) and \( k \) from eq. (66), the normalizing condition, and \( k \) of unity, which for simplicity we denote as the vector \( \mathbf{T} \), we can plug into

\[
\begin{align*}
0 &= g_x(1) - g_x(1) + \Delta g_x(1) \Delta A + \Delta g_x(1) \Delta B + \Delta g_x(1) \Delta C + \Delta g_x(1) \Delta k \\
0 &= g_y(1) - g_y(1) + \Delta g_y(1) \Delta A + \Delta g_y(1) \Delta B + \Delta g_y(1) \Delta C + \Delta g_y(1) \Delta k \\
0 &= g_z(1) - g_z(1) + \Delta g_z(1) \Delta A + \Delta g_z(1) \Delta B + \Delta g_z(1) \Delta C + \Delta g_z(1) \Delta k \\
0 &= A^2 + B^2 + C^2 - 1 + 2A \cdot \Delta A + 2B \Delta B + 2C \Delta C + 0
\end{align*}
\]

The correction vector \( \Delta \) to the estimate vector \( \mathbf{T} \) is given by \( \Delta = (\Delta A, \Delta B, \Delta C, \Delta k) \), and is obtained by solving the linear system given in (72).
The criterion we used for convergence was when the sum of the squares of the right hand side of Eq. (69) was less than $1 \times 10^{-15}$, the system had converged. If, however, the system failed to converge in less than 50 iterations, the result was noted on the computer print out.

Once the form of the ground electronic wavefunction has been determined, the next step is to obtain the crystal field parameters and the energy of the ground state relative to the unsplit $^2T_2$ state. By using the secular equation $\mathbf{H} \psi = E_1 \psi$ as determined earlier gives three equations and three unknowns, from (13),

\[
\begin{align*}
E_1/\lambda + D/\lambda - 3EC/\lambda A &= -1/2 - B/\sqrt{2}A \\
E_1/\lambda - 2D/\lambda &= -A/\sqrt{2}B \\
E_1/\lambda + D/\lambda - 3EA/\lambda C &= 1/2
\end{align*}
\]

This set of equations can then be solved to obtain $D/\lambda$ and $E/\lambda$, the crystal field parameters, and $E_1/\lambda$, the energy of the ground state, relative to the spin orbit coupling constant.

The criteria for choosing the correct set of coordinate axes are: 1) the left hand side of Eq. (66) should not deviate from unity by more than 10 percent, 2) after the final wavefunction is determined, $k$ should have a value which is "reasonable." Using Herrick and Stapleton's [62] data for P450, the value of $k = 1.146, 1.151, -2.150, -2.235$. The last two values are not reasonable. It should
be noted that for the last two values, condition (1) was not met. 3) E must be positive, and $|E/D|$ should be as small as possible [49].

The above calculation is done by a program GVAL (Appendix II) and output from the program is given in tables 2 and 3 for P450 and LOW, respectively.

Now that the crystal field parameters are known, the Hamiltonian in Eq. (12) can be solved and the three energy levels obtained, the theoretical g values and A tensor determined and the valence contributions to the EFG calculated. This is done in the program QSPLIT in a very straightforward fashion (Appendix III).

Using D,E, and $\lambda$, the matrix for the Hamiltonian, given in Eq. (13) is calculated and diagonalized by the IMSL subroutine EIGRS [64]. Once the form of the wavefunction and its energy for each doublet is known, the g-tensor, A-tensor, and EFG can be calculated as well as the temperature dependence of the EFG. This is accomplished with Eqs. (36)-(39) and (46). It should be noted at this point that this assumes that the g-tensor, the EFG and the A-tensor all are co-axial. Further, the parameters $N_{xy}$, $N_{xz}$, and $N_{yz}$, while having physical significance, allow the adjustment of the calculated EFG and A-tensor to fit the experimental data and could be thought of as "fudge factors."

The calculation of the Mossbauer spectra based on the relaxation theory of IIID is calculated using the routine
Table 2. Using the g values of cytochrome P-450 from Herrick and Stapleton [62], all possible permutations of the g tensor which will yield a real ground electronic state eigenvector, the calculated eigenvector coefficients and the appropriate crystal field parameters.
<table>
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<th>GX</th>
<th>GY</th>
<th>GZ</th>
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<th>A</th>
<th>B</th>
<th>C</th>
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**Note:** The image appears to contain technical data and calculations, possibly related to engineering or physics, but the specific details are not clear due to the resolution and orientation of the image. The table includes various numerical values and equations, typical of a scientific or technical report.
of G. K. Shenoy of Argonne Labs [65]. The main body of the
calculation was done using this routine with modifications
and corrections added locally. The method follows the
theory of section IIID. In the calculation of the relaxa-
tion part of the problem, the relaxation rate $VJ_2$ is a
phenomenological factor like the covalency factors, which
allows us to adjust the theory to fit the data. A complete
calculation of relaxation rate from first principles is not
possible with available information about the electronic
levels in $\text{LOW}$.

The calculation of the polycrystalline EPR spectrum is
straightforward but complex. The computation may be accom-
plished by two methods, both of which ultimately yield the
same results. It is illustrative to first discuss the
problem in terms of rotations of the $g$-tensor and progress
from there to the closed form solution which we currently
use.

First it is necessary to define a cartesian coordinate
system or laboratory axis system. We shall align the mag-
netic field $\vec{H}$ along the $z$ axis and have the fluctuating
microwave field $\vec{H}_1 \cos \omega t$ acting as a perturbation along
the $x$ axis. Then in terms of a spin Hamiltonian, the inter-
action is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = \vec{H} \cdot \vec{g} \cdot \vec{S} + \vec{H}_1 \cdot \cos \omega t \cdot \vec{g} \cdot \vec{S}$$  \hspace{1cm} (74)

for an $S = 1/2$ system, and ignoring hyperfine interactions.
This Hamiltonian will operate on a basis of $|s, m_s> = |1/2, 1/2> \text{ and } |1/2, -1/2>$. 

When the $g$ tensor is aligned with the laboratory axis system then the $g$ tensor is given by

$$
\tilde{g} = \begin{pmatrix}
g_x & 0 & 0 \\
0 & g_y & 0 \\
0 & 0 & g_z
\end{pmatrix}
$$

(75)

For a $g$ tensor not aligned along the laboratory axis system, a rotation operator $\tilde{R}(\psi, \theta, \phi)$ can be defined such that

$$
\tilde{R}(\psi, \theta, \phi) = \tilde{R}(\psi) \tilde{R}(\theta) \tilde{R}(\phi)
$$

(76)

where $\psi$ is a screw rotation around the z axis, $\theta$ is the polar angle, and $\phi$ is the azimuthal angle and

$$
\tilde{R}(\psi) = \begin{pmatrix}
\cos \psi & -\sin \psi & 0 \\
\sin \psi & \cos \psi & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

(77)

$$
\tilde{R}(\theta) = \begin{pmatrix}
\cos \theta & 0 & \sin \theta \\
0 & 1 & 0 \\
-\sin \theta & 0 & \cos \theta
\end{pmatrix}
$$

(78)

$$
\tilde{R}(\phi) = \begin{pmatrix}
\cos \phi & -\sin \phi & 0 \\
\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

(79)
Since the magnetic field is along the z axis in the laboratory frame, the magnetic field vector is given by

\[ \vec{H} = \begin{pmatrix} 0 \\ 0 \\ H_z \end{pmatrix} \]  

(80)

Thus, for a general orientation of the g tensor relative to our laboratory axis system, our Zeeman interaction becomes

\[ \mathcal{H}_O = H_z \vec{R} \vec{g}_T \cdot \vec{S} \]  

(81)

The resulting 2 x 2 matrix for this Hamiltonian can then be diagonalized to yield energy levels split by

\[ \Delta E = g_{\text{eff}} \cdot \beta \cdot H_{\text{eff}} \]  

(82)

where

\[ g_{\text{eff}}^2 = g_x^2 \sin^2 \theta \cos^2 \phi + g_y^2 \sin^2 \theta \sin^2 \phi + g_z^2 \cos^2 \theta \]  

(83)

and

\[ H_{\text{eff}} = \hbar \omega/g_{\text{eff}} \cdot \beta \]  

(84)

where \( \omega \) is the microwave frequency and \( \beta \) is the Bohr magneton and is independent of \( \psi \).

If we represent the eigenvector of this operator as

\[ |\psi^+\rangle = a_{\pm}|+1/2\rangle + b_{\pm}|-1/2\rangle \]  

(85)
we can use this eigenfunction to calculate the transition probability for a given transition for a given orientation. The transition probability is given by

$$I = |\langle \psi^+ | H_1 | \psi^- \rangle|^2 \quad (86)$$

A closed form solution to this problem has been worked out by Pilbrow [66]. In this case, the general orientation of the magnetic field $H$ relative to a fixed $g$ tensor is given by the standard spherical polar coordinate angles $\theta'$ and $\phi'$. The intensity of an arbitrary orientation specified by $\theta'$ and $\phi'$ is given by

$$I^2 = [g_x^2 g_y^2 \sin^2 \theta' + g_y^2 g_z^2 (\sin^2 \phi' + \cos^2 \theta' \cos^2 \theta')]$$

$$+ g_z^2 g_x^2 (\cos^2 \phi' + \cos^2 \theta' \sin^2 \phi')] / 2 g_{\text{eff}}^2 \quad (87)$$

where $g_{\text{eff}}$ has been previously defined in Eq. (83).

Since the angles enter into this formula as the squares of the sine and cosine terms, the fact that $\theta' = -\theta$ and $\phi' = -\phi$ does not have any effect on the problem and the calculation for polycrystalline spectrum can be obtained by a numerical integration over all possible orientations of $\theta$, $\phi$. This is performed in our program MULTEPR in Appendix V, which allows for linear combinations of the spectra based on a weighting factor and a normalized area of the spectra.
V. EXPERIMENTAL RESULTS

A. Mossbauer Data

The spectra presented in this thesis are based on four samples of Fe(TPP)(S\$)(HS\$). Two samples, SRL2 and SRL6, were prepared by Dr. T. N. Sorrell at Stanford. The other two samples, SRL12 and SRL14, were prepared locally by Dr. W. E. Silverthorn. The Mossbauer spectra for these samples as a function of temperature are shown in Figs. 5-8. A fifth sample, SRL4, is the same material as SRL2, but allowed to decompose by sitting in a covered evaporating dish for a period of several weeks, Fig. 9. Because of reported instability of the material [14, 67], the materials were stored under dry ice or liquid nitrogen when not in use to minimize decomposition. The SRL2 data was obtained over a period of four weeks with no apparent decomposition due to storage while other data was collected. If the sample is held at room temperature for prolonged periods, its spectrum changes, with an increase in the relative abundance of a component resembling the decomposed material in Fig. 9.

B. Magnetic Susceptibility Data

The effective magnetic moment as a function of temperature for sample SRL12 is given in Fig. 10. An 11 mg
Figure 5. Mossbauer spectra of Fe(TPP)(S\(^{+}\))(HS\(^{-}\)) as a function of temperature (temperature in K). Material from T. Sorrell.
Figure 6. Temperature dependent Mossbauer spectra of Fe(TPP)(Sφ)(HSφ). Sample from T. Sorrell.
Figure 7. Temperature dependent Mossbauer spectra of Fe(TPP)(SΦ)(HSΦ). Sample from W.E. Silverthorn.
Figure 8. Temperature dependent Mossbauer spectra of SRL 14 both in and out of a magnetic field.
Figure 9. Temperature dependent Mossbauer spectra of SRL 2 allowed to decompose on air. Spectra are typical of high-spin ferric porphyrin.
sample was run as described in Section IIC. Since the apparatus has been available for a short time, only one set of data was obtained. However, Sorrell [67] reports results similar to that shown in Fig. 10 for samples synthesized in that laboratory. The diamagnetic correction of 431.4 x $10^{-6}$/mole was calculated from the usual atomic susceptibilities [68].

C. Electron Paramagnetic Resonance Data

The EPR spectra of sample SRL12 as a function of temperature is given in Fig. 11. Since the material was not perfectly polycrystalline, the relative intensity of the peaks is slightly orientation dependent. The data in Fig. 11 is reproducible over the entire temperature range, with slight relative intensity changes among the different samples. The actual g values were obtained from 4.22 K spectra taken over the range 2600 G to 3600 G which yielded better peak resolution.
Figure 10. Effective magnetic moment of SRL12 as a function of temperature.
Figure 11. EPR spectra of SRL12 as a function of temperature. Temperature in K. Microwave frequency for temperature 4.2 to 275 K is 9.145 GHz, at 300 K \( \nu = 9.531 \text{ GHz} \). The \( g \) values on the graph are for \( \nu = 9.145 \text{ GHz} \).
VI. DATA ANALYSIS

A. Mossbauer Spectra

The Mossbauer data for Fe(TPP)(S\$)(HS\$) can be resolved into three distinct components. Two are low spin components, one labeled RLX due to the relaxation model necessary to describe it, and one labeled IMP, because initially it was thought to be an impurity. The high spin component is labeled HI. The quadrupole splitting, \( \Delta E_Q \), and isomer shift, \( \delta \), for the three components at selected temperatures are listed in Table 4. This data is based on non-linear least squares fits [69, 70] of the data to a model composed of the sum of several Lorentzians, with each component being represented by two peaks (Appendix VI). Data for absorbers in the presence and absence of a magnetic field was used to prepare Table 4.

The component RLX consists of two peaks at approximately -0.10 cm/sec and +0.18 cm/sec and is a very asymmetric doublet. The left peak is a broad low intensity peak with a full width at half maximum of 0.084 cm/sec while the right peak is narrower and of greater intensity, with a half width of 0.052 cm/sec. It is usual to assume that a pair of peaks in a quadrupole doublet can be represented by four parameters, a common intensity, a common half width, and two positions. When the doublet is asymmetric, the
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Component</th>
<th>RLX</th>
<th>IMP</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E_1$ (cm/sec)</td>
<td>$\delta_1$ (cm/sec)</td>
<td>$\Delta E_2$ (cm/sec)</td>
<td>$\delta_2$ (cm/sec)</td>
</tr>
<tr>
<td>4.22 K</td>
<td>0.282±0.003</td>
<td>0.038±0.003</td>
<td>0.175±0.003</td>
<td>0.053±0.003</td>
</tr>
<tr>
<td>77</td>
<td>0.274</td>
<td>0.037</td>
<td>0.172</td>
<td>0.054</td>
</tr>
<tr>
<td>130</td>
<td>0.278</td>
<td>0.038</td>
<td>0.178</td>
<td>0.054</td>
</tr>
<tr>
<td>175</td>
<td>*</td>
<td>*</td>
<td>0.174</td>
<td>0.055</td>
</tr>
<tr>
<td>250</td>
<td>*</td>
<td>*</td>
<td>0.169</td>
<td>0.061</td>
</tr>
</tbody>
</table>

*not resolved
half widths and intensities of the two peaks will usually be related, such that both peaks will have the same area. Attempts to fit the RLX component to either of these constraints failed to match adequately the data. This, however, is consistent with the relaxation model used to fit the data and explained later.

The component IMP is a symmetric quadrupole doublet with one peak at -0.03 cm/sec and the second at +0.14 cm/sec. The quadrupole splitting of P-450 is 0.285 cm/sec [7] and low spin ferric porphyrins have quadrupole splittings of +0.17 to +0.36 cm/sec [10, 21]. The intermediate spin ferric case has not been observed in porphyrin complexes, however, in smaller tetraaza macrocyclic complexes it is observed, yielding quadrupole splittings in the range +0.19 to +0.25 cm/sec [20]. Thus, while the quadrupole splitting of the IMP component is lower than most low spin ferric porphyrins, it is not unreasonable to consider IMP to be a low spin form. Further, as noted below, the EPR data suggests that the component is low spin. The evidence for treating IMP as a symmetric doublet is given in Fig. 12. This shows the difference between two different samples at the same temperature. Each component was weighted by an appropriate factor to minimize the difference of the RLX component in the two spectra. The relative amounts of components IMP and RLX varied greatly from sample to sample. Absorbers prepared by different techniques using the same
Figure 12. Difference spectrum (center) of selected Mossbauer spectra at the same temperature. Weighting factors used in taking the difference were chosen to minimize the RLX component (4.2 K to 110 K) or minimize the HI component (150 K to 250 K). This shows IMP to be a symmetric quadrupole doublet.
sample yielded identical Mossbauer patterns. Due to the excellent analysis of the material we feel that the presence of two magnetic environments for Fe$^{\text{III}}$ is a property of the material.

The component HI consists of an asymmetric pair at 0.02 cm/sec and 0.07 cm/sec. These peak positions are consistent with both the P450 enzyme and a large body of other high-spin ferric porphyrins [7, 13, 21, 71]. The Mossbauer spectra of high spin porphyrins is complicated by two factors. First, the relative intensities of the two quadrupole peaks can vary as a function of temperature, and in some cases, the asymmetry can actually reverse [13]. Second, in weak magnetic fields, the spectra can be split, and the doublet will be replaced by a complex multi-line pattern [51, 71].

The Mossbauer data strongly suggest that there are actually two high spin components represented by the two peaks labeled HI. In the temperature range 200-250 K, there is no evidence for the existence of significant amounts of the RLX component. If there were only two components remaining, the IMP component and one high spin component, then the Mossbauer spectra from various samples at the same temperature would be fit to a common set of parameters, with only the relative abundance of the two components varying. The IMP component can be fit to this criterion, but
the HI component cannot, indicating that there are actually two components present. These two components, however, cannot be resolved due to super-position of their respective patterns. Recent structural evidence from Strouse supports the concept of more than two components in a single sample [72].

The effect of an externally applied magnetic field is to cause the components RLX and HI to become better resolved doublets. Fig. 14 shows the difference of two spectra of the same sample at various temperatures, both in and out of a polarizing field. The difference spectrum shows that the RLX component is becoming sharper and better resolved, and, except at 4.2 K, also shows improvement in the resolution of the HI component. No change is noted in the IMP component. It should also be noted that the contribution from the RLX spectra at 150 K is very small, but present.

The temperature dependence of the relative abundance of the RLX and IMP components is attributed to a gradual spin transition of the low spin form to the high spin form, accompanied by a crystallographic transition [15]. If it is assumed that the recoil free fraction of each component is the same, then by taking areas under each pair of peaks, the percent composition can be obtained. When the relative abundance of the IMP component is plotted as a function of temperature, the curve goes through a peak at about 150 K.
Figure 13. Mossbauer spectra of a sample both in and out of a polarizing magnetic field. Difference spectrum is shown in the middle.
Since a crystallographic phase transition is involved in which the central ion shifts from an in-plane low spin form to an out-of-plane high spin form, it would be expected that the recoil free fraction of the components involved in this transition would decrease and the apparent percent composition drop.

The first transition is from a low spin (RLX) component to a high spin component. As temperature is further increased, the second low spin component IMP also is transformed to a high spin component. This is supported by the difference spectra in Fig. 12. When the contribution due to RLX is eliminated, the component HI is also eliminated in the low temperature spectra (T < 150 K). Thus, up to 150 K, the IMP component has not started to convert. At temperatures of 150 K and above, the HI component is used for the scaling in Fig. 12 and it is difficult to determine when the transition starts.

B. EPR and Susceptibility Measurements

The polycrystalline EPR spectra of rhombic low spin ferric compounds are characterized by three g values, one at approximately $g = 2.9$ to $2.3$, one at $g = 2.3$ to $2.2$, and one at $g = 1.97$ to $1.90$ [11, 21, 61]. In axial symmetry, the high spin ferric EPR spectrum for a polycrystalline sample is characterized by a spectra with $g_x = g_y = 6$ and a weak resonance at $g_z = 2$. When the symmetry is decreased
(E ≠ 0 in Eq. (21)), the g = 6 resonance splits up and can yield resonances in the range 6 to 8 for g_y and 3.7 to 5.5 for g_x [48]. Intermediate (S = 3/2) spin ferric complexes usually exhibit a very broad resonance in the g = 4 range [73].

The temperature dependent EPR spectra of Fe(TPP)(S0 (HS)) shows a set of lines at g = 2.363, 2.240, and 1.965, based on the 4.2 K spectrum. As temperature is increased, peaks at g = 8.7 and 6.4 begin to appear, along with a broad resonance in the g = 4.5 to 3.5 range. At temperatures above 200 K, a resonance at g = 2 also begins to appear.

The susceptibility data for SRL12 (Fig. 10) shows a gradual change from low spin to high spin with the spectrum approaching the S = 5/2 spin only value of \( \mu_{\text{eff}} = 5.92 \). The magnetic moment is expected to vary from sample to sample since the low spin fraction at a given temperature varies from sample to sample.

In the temperature range 30 K to 50 K, the leveling out of \( \mu_{\text{eff}} \) corresponds to the region where the relative intensities of the g = 2.36 and 2.24 peaks change. This may be evidence of magnetic exchange.

C. Correlation of EPR and Mossbauer Data

Although the quadrupole splitting in the IMP component is somewhat low for a S = 1/2 ferric ion, the EPR spectra indicate that it must be a low spin contribution. The
major component of the EPR at 4.2 K is due to the low spin ferric component with minor ripples in the low field region due to a small amount of high spin impurity in the sample. Although the relative intensities of the lines and the line widths change as a function of temperature, this low spin contribution is still present in the EPR at 300 K. The decrease in intensity of this component closely parallels the decrease in intensity of the IMP component in the Mossbauer. Further, since there are two predominant components, RLX and IMP in the 4.2 K Mossbauer spectrum, and only one major spectral component in the EPR at the same temperature, it can be concluded that both of these components in the Mossbauer give rise to the same low spin EPR signal. The increase in linewidth of the low spin EPR spectrum is consistent with this conclusion. The broadened lines at higher temperatures in the EPR suggest a fast relaxation case, which would give rise to a symmetric doublet in the Mossbauer spectrum, which is what is observed for the IMP component.

To calculate theoretically the spectrum of the RLX component, we must first obtain the ground state wavefunction, and using that wavefunction, calculate the experimentally observed variables. Using the modulus of the g-values obtained from the 4.2 K EPR spectrum, the coefficients of the low spin wavefunction (Eq. 14) can be determined.

From Table 3 we find that the criteria for a correct set
of coordinate axes are met by the sets \( g = -2.363, 2.240, -1.965 \), and \( g = -2.363, 2.240, 1.965 \). These sets of \( g \) values differ by the sign of the product \( g_x g_y g_z \). Since we do not know the sign of this product, we choose the former set based on the following criteria. First, the deviation of ANORM from unity is minimized, and second, the sign of the product of \( g_x g_y g_z \) is positive for most similar biological systems where the sign has been determined [61]. Further, this sign choice agrees with the EPR results for P450 reported by Herrick and Stapleton [62]. The coefficients of the electronic wavefunction and crystal field parameters for both P450 and LOW are given in Table 5.

Using the \( g \)-values obtained from the 4.2 K EPR spectrum, the theoretical polycrystalline EPR spectrum can be calculated and is shown in Fig. 15. This spectrum compares well with the experimental result.

Now that the ground electronic wavefunction has been determined, a theoretical Mossbauer pattern can be calculated using the operator in Eq. (51). We must now determine a set of physically reasonable values for the various parameters which will reproduce the experimental spectra. Since the high spin component is not well resolved at 4.2 K and, as previously mentioned, extensive studies of other high spin porphyrin derivatives demonstrate the complexity of the temperature dependent behavior of the high spin porphyrins, the 77 K spectra will be simulated. The electric
Table 5. Crystal field parameters and wave function coefficients calculated from EPR g tensor for LOW and P-450 (P-450 data from [62]).

<table>
<thead>
<tr>
<th>Sample</th>
<th>D/λ</th>
<th>E/λ</th>
<th>Crystal Field Parameters</th>
<th>g&lt;sub&gt;x&lt;/sub&gt;</th>
<th>g&lt;sub&gt;y&lt;/sub&gt;</th>
<th>g&lt;sub&gt;z&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-450</td>
<td>-2.34966</td>
<td>0.52284</td>
<td>E/D -0.22252 k 1.1463</td>
<td>-2.417</td>
<td>2.249</td>
<td>-1.921</td>
</tr>
<tr>
<td>LOW</td>
<td>-3.65370</td>
<td>0.71284</td>
<td>E/D -0.19510 k 1.58342</td>
<td>-2.363</td>
<td>2.240</td>
<td>-1.965</td>
</tr>
</tbody>
</table>

Coefficients of the Wavefunction  

<table>
<thead>
<tr>
<th>i</th>
<th>Ai</th>
<th>Bi</th>
<th>Ci</th>
<th>(E&lt;sub&gt;i&lt;/sub&gt;-E&lt;sub&gt;i&lt;/sub&gt;)/λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.06974</td>
<td>-0.99748</td>
<td>-0.01296</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-0.77801</td>
<td>0.06252</td>
<td>0.62513</td>
<td>8.849</td>
</tr>
<tr>
<td>3</td>
<td>0.62437</td>
<td>-0.03352</td>
<td>0.78041</td>
<td>13.221</td>
</tr>
<tr>
<td>1</td>
<td>0.1116</td>
<td>0.9935</td>
<td>-0.0229</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.7954</td>
<td>-0.1031</td>
<td>-0.5972</td>
<td>5.533</td>
</tr>
<tr>
<td>3</td>
<td>0.5957</td>
<td>-0.0484</td>
<td>0.8017</td>
<td>8.778</td>
</tr>
</tbody>
</table>
Figure 14. Simulated EPR spectrum of the low-spin contribution (LOW) of Fe(TPP)(S⁺) (HS⁺). The dashed line is the absorption spectrum and the solid line is the derivative spectrum.
field gradient is dependent on the coefficients of the electronic wavefunction and the covalency factors. The hyperfine tensor is dependent on the coefficients of the wavefunction, the covalency factors, \( \kappa \), and \( P \).

In order to limit the number of parameters used in fitting a relatively simple spectrum, certain limits were imposed. Since the hyperfine tensor was relatively insensitive to the covalency factors, these factors are chosen to give the best fit of the calculated electric field gradient to the experimental result. This necessitated two assumptions: first, that the only contribution to the electric field gradient was the valence contribution, and second, that \( \frac{e^2 q_0}{4} = 1.5 \times \frac{7}{<r^{-3}>} q_{\text{val}} \text{ mm/sec} \) gives the result \( N_{xy}^2 = .95 \) and \( N_{xz}^2 = N_{yz}^2 = .80 \).

This choice of covalency factors can be justified by two arguments. First, these values are similar to the values chosen for P450 by Sharrock, et al. [7], and second, they are consistent with the Huckel calculations of Zerner [74] on iron porphyrins. Griffith [44] argues that the anisotropy in the covalency factors is reasonable due to the \( \pi \) bonding interactions of the \( d_{xz} \) and \( d_{yz} \) orbitals with the porphyrin ring, while the \( d_{xy} \) orbital will be fairly well away from the area in which the ligand electron density is concentrated. This would also explain why the \( d_{xy} \) orbital is lowest in energy. A small displacement of the iron out of the porphyrin plane would tend to further
increase the stability of the $d_{xy}$ orbital relative to the $d_{xz}$ and $d_{yz}$ orbitals [7].

To calculate the Mossbauer spectrum, we must fix three final parameters: the relaxation rate constant $VJ2$, where $VJ2 = \beta^2 J_q$ in Eq. (63); the effective field at the nucleus, $PK/g_n\beta_n$; and the Fermi contact constant, $\kappa$. By allowing $PK/g_n\beta_n$ to range from 190 to 220 kilogauss and varying $VJ2$ within that limit we found that $\kappa = 1.58$ would not yield acceptable results but $\kappa = 0.625$ produced a more acceptable result. Although we expected $k \sim \kappa$, this result is not alarming. Lang and Marshall determined $\kappa = 0.35$ for low spin ferric heme complexes. A low value for the Fermi contact constant yields a highly anisotropic $A$ tensor. A higher value of $\kappa > 1$ would have yielded an almost isotropic $A$ tensor. In cases where hyperfine structure is resolved, the $A$ tensor is usually highly anisotropic. The final parameters are given in Table 6. Figs. 16 and 17 show theoretical Mossbauer spectra calculated from these parameters. Fig. 16 shows the variation of the spectrum as a function of relaxation rate, $VJ2$. Fig. 17 shows the building up of the three components to simulate the data using the relaxation spectrum from Fig. 16.

The temperature dependence of $\eta$ and $e^2qQ/4$ of the RLX component is described by the Boltzmann sum in Eqs. (38) and (39). By assigning a value of 688 cm$^{-1}$ to $\lambda$, which is $k$ times the free ion value of Weissbluth [75], we find that
Table 6. Parameters used in simulating Mossbauer spectra for P-450 and LOW (P-450 data from [7]).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>P450</th>
<th>LOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_x$</td>
<td>1.91</td>
<td>-2.363</td>
</tr>
<tr>
<td>$g_y$</td>
<td>2.26</td>
<td>2.240</td>
</tr>
<tr>
<td>$g_z$</td>
<td>2.45</td>
<td>-1.965</td>
</tr>
<tr>
<td>$A_{xx}/g_n\beta_n$ (KG)</td>
<td>-450</td>
<td>43</td>
</tr>
<tr>
<td>$A_{yy}/g_n\beta_n$ (KG)</td>
<td>102</td>
<td>-71</td>
</tr>
<tr>
<td>$A_{zz}/g_n\beta_n$ (kG)</td>
<td>191</td>
<td>340</td>
</tr>
<tr>
<td>$N_{xy}$</td>
<td>0.96</td>
<td>0.95±0.05</td>
</tr>
<tr>
<td>$N_{xz}$</td>
<td>0.80</td>
<td>0.80±0.1</td>
</tr>
<tr>
<td>$N_{yz}$</td>
<td>0.80</td>
<td>0.80±0.1</td>
</tr>
<tr>
<td>$\Delta E_Q$ (cm/sec)</td>
<td>0.285</td>
<td>-2.282</td>
</tr>
<tr>
<td>$\eta$</td>
<td>-1.80</td>
<td>0.0</td>
</tr>
<tr>
<td>$eQV_{zz}/4$ (cm/sec)</td>
<td>0.099</td>
<td>-0.141</td>
</tr>
<tr>
<td>$\delta$ (cm/sec)</td>
<td>0.038</td>
<td>0.038</td>
</tr>
<tr>
<td>$\Gamma$ (linewidth in cm/sec)</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td>$VJ2$ (MHz)</td>
<td>--</td>
<td>45±5</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>1.14</td>
<td>0.625±0.025</td>
</tr>
</tbody>
</table>
Figure 15. RLX using parameters from Table 6 as a function of the relaxation rate constant VJ2.
Figure 16. The three components which are summed to simulate the spectra of Fe(TPP)(HSϕ)(Sϕ). Parameters for HI and IMP from Table 4. Parameters for RLX from Table 6.
\(\eta\) and \(e^2 qQ/4\) should be temperature independent over the range 0 to 300 K. This agrees well with the experimentally determined results.
VII. CONCLUSIONS

We have presented evidence that there are four distinct magnetic environments for iron in Fe(TPP)(S\theta)(HS\phi), two low spin and two high spin. The low spin forms undergo a gradual magnetic spin transition to the high spin form. The transitions occur over different temperature ranges, with the RLX component transforming over the range 100 to 200 K and IMP transforming over the range 200 to 300 K. These transformations are similar in nature to the temperature dependent transformations of substrate bound ferric P450 [7]. In P450, the high spin fraction will increase from 50% to 70% as the temperature is raised from 4.2 K to 220 K. The reason for the incomplete conversion is unknown.

An acceptable fit of the theoretical relaxation model to the experimentally determined spectra has been shown. However, the simulated spectrum for RLX is relatively simple and not very sensitive to the input parameters. This limits somewhat our ability to achieve a unique fit. This problem might be resolved by magnetically perturbed Mossbauer measurements using polarizing fields of greater strength than were available in this work. However, due to the number of components present in the sample, the spectrum would be complex.

The EPR g values observed for LOW are very similar to the g values observed for a wide range of six coordinate
ferric porphyrin complexes where sulfur is one of the axial ligands [14, 21]. The nature of the spin transition, and to a lesser extent, the electric field gradient, are more sensitive to slight changes in axial ligation. In the model compound, the nature of the axial ligands is known, however, the positions of the axial sulfurs relative to the ferric iron is not well established. Recent work by Strouse [72] indicates that two different structural species exist at all temperatures over the range 90 to 300 K with some variation in relative abundance of each component as a function of temperature. The two species are similar to those found in previously published work (Fig. 2) [15]. At 4.2 K, each of the two low spin components would correspond to one of the two structural species. It would be reasonable to assume that the relative abundance of each of the two structural species would vary from sample to sample depending on the crystallization conditions. This is supported by the data from a recrystallized sample of SRL6 which shows a different ratio of RLX to IMP.

Although most of the low spin ferric porphyrins are six coordinate, this is not always the case. Smaller six coordinate ferric tetraaza macrocycles with sulfur as the axial ligands exhibit all three possible spin states, with the spin state depending on the exact nature of the ligation for six coordinate species [20]. At least one example of a five coordinate low spin ferric porphyrin has been reported [22].
Thus it is not unreasonable at 4.2 K to assign the two low spin magnetic components IMP and RLX to the two structural species found by Strouse even though in one of the species the iron is five coordinate. It is further reasonable to attribute the two high spin components to these same structural species at room temperature by assuming that a spin transition occurs. Most low spin to high spin transitions are accompanied by a structural transition, however, this is not always the case [43].

Two factors govern the nature of the spin transition in ferric porphyrins. First, the interaction of the various spin states with one another. The stronger this interaction, the sharper or more abrupt the transition [76]. Second, the exact nature of the ground state will be strongly dependent on the difference between the bonding of the iron to the ring contrasted with the bonding to the axial ligands [77]. Therefore, the critical temperature, $T_c$, and the rate of conversion from low spin to high spin as a function of temperature would differ between the two structural species.

Strouse has further suggested the possibility of interconversion of the two structural species [72] which would account for the increase in the relative abundance of the IMP component at temperatures near 150 K. Cases have been reported where one species, such as RLX, converts to two species rather than just one as temperature is increased
[78]. We cannot at this time, however, assign the different magnetic components to the appropriate structural species.

The present study is then of interest for two reasons. First, the compound is interesting in its own right, due to the large number of magnetic environments and the transitions the ions undergo. Second, since the $g$ tensor for LOW is similar to that of P450, sulfur is probably involved in at least one axial ligation site on the P450 enzyme. Further study would be useful to obtain materials which are fully converted to either of the low spin forms exhibited here.
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APPENDICES
APPENDICES

The following seven programs were used to analyze and display the data presented in this thesis. Various subroutines from locally available libraries were used in these programs and are listed below.

COMPlot Library [79, 80] - used for plotting on X-Y drum and bed plotters

- **AXIS** draws X-Y axis system
- **PLOT** draws a data mark at point X,Y
- **PLOTEND** terminate plot and move to new plot region
- **POINTS** causes PLOT subroutine to draw only data marks
- **SIZE** defines size of plot region
- **SCALE** defines plotting region in users units
- **SYMBOL** prints labels on plot
- **VECTORS** causes PLOT subroutine to connect data marks with a line

IMSL Library [64]

- **EIGCC** calculates eigenvalues and eigenvectors for a complex general matrix
- **EIGRS** calculates eigenvalues and eigenvectors for a real symmetric matrix
- **LEQTIF** solves linear equations
- **VCVTFS** places matrix into symmetric stragic mode for EIGRS

LPPLTLB Library - line printer plotting library

- **AXIS** draws X-Y axis on line printer
- **PLOT** plots an array of X,Y pairs
LABLPLT  labels plot

KEITHLB library

LABELP  routine for creating a label card on the card punch
APPENDIX I

Programs MOSSRED and SWMPLLOT
PROGRAM MOSSRED
C
REVISION NO. 4, 21 JULY 1976
C
THIS PROGRAM NORMALIZES AND PLOTS NO-2400 RAW DATA. THE LATTER
HAS PREVIOUSLY BEEN READ FROM PAPER TAPE AND STORED ON DISC FILES
LABELED BY THE EXPERIMENTAL DESCRIPTOR (EG. OT49). UP/COWN
MULTI-SCALING IS ASSUMED SO NO FOLDING OPTIONS EXIST.
LOGICAL UNITS USED BY MOSSRED.

LUN 10 = PLOTTER
LUN 15 = LINE PRINTER
LUN 16 = PUNCH

THESE LUNS MUST BE EXTERNALLY EQUIPEC AND LABELED BEFORE
RUNNING THE PROGRAM.

LUN 20 = DATA

THIS FILE IS INTERNALLY EQUIPEC BY THE PROGRAM AND THEREFORE
MUST BE FREE.

THE FOLLOWING SYMBOLS ARE THE INPUT PARAMETERS TO THE PROGRAM.

N=NUMBER OF INITIAL POINTS TO BE READ. IF N IS GREATER
THAN 1200, THE PROGRAM ENDS.
IF N = 0, THE PROGRAM USES THE OPTION TO GENERATE A PLOT
(ONLY) FROM OUTPUT CREATED BY THIS PROGRAM, AND READS
THE DECKS PRODUCED.
ND=NUMBER OF INITIAL POINTS TO BE DELETED.
NDLY=NUMBER OF DELAY PULSES.
OVP=NUMBER OF OVERFLOWS.
CG=CENTROID OF SPECTRUM.
VELC=CALIBRATION CONSTANT IN MM/SEC/CH.
NOPT=OPTIONAL PLOT FLAG. IF NOPT IS NON-ZERO THE
OPTIONAL PLOT IS GENERATED. IF NOPT IS ZERO
THE OPTIONAL PLOT IS NOT GENERATED.
TEXT=AN ARRAY OF DIMENSION 9 WHICH IS THE TITLE FOR THE PLOT.
TEXT(1) MUST CONTAIN THE EXPERIMENTAL DESCRIPTOR LEFT
JUSTIFIED.
FLAG=OPTIONAL FLAG. IF FLAG IS ONE THE BACKGROUND OF MOSSBAUER
SPECTRA IS CORRECTED FOR SLOPE BY PATIO METHOD.

*****NOTE! FLAG IS AN INTEGER VALUE (IMPORTANT)******

IF CG AND VELC ARE NON-ZERO THE PLOT WILL CONTAIN AN ABSCISSA
IN CHANNEL UNITS AND AN ADDITIONAL ABSCISSA IN UNITS OF MM/SEC.

INPUT:
TO RUN THE PROGRAM, THE FILE(S) TO BE USED MUST EXIST AND
HAVE BEEN EDITED AND STORED UNDER THE NAME OF THE EXPERIMENTAL
DESCRIPTION. ALL TITLES, COMMENTS, AND EXTRA CHANNEL COUNTERS MUST
HAVE BEEN REMOVED FROM THE FILE, SINCE THE PROGRAM READS ONLY
THE DATA FROM THIS FILE.
IF A RE-PLTO OF ANY NORMALIZED SPECTRA IS DESIRED, THE ABOVE INSTRUCTIONS ARE
NOT USED. THE METHOD USED TO RE-PLTO SUCH DATA DEPENDS ON WHETHER AN
AUTOSCALING CARD EXISTS WITH THE DATA: WITH AUTOSCALING CARD THE VALUES OF
CG, VELC, AND AN ADDITIONAL VELOCITY AXIS ARE PRESENT. WITHOUT AUTOSCALING
CARD THE USER MUST CREATE AN AUTOSCALING CARD WITH THE FOLLOWING VALUES
YMAX=1.1, YMIN=0., CG=0., VELC=0., NTOT, AND NZERO. THE VALUES OF CG, VELC,
AND ADDITIONAL VELOCITY AXIS ARE NOT PRESENT. THIS METHOD WILL PRODUCE AN
AUTOSCALING CARD AND A LABEL CARD.
THE VALUES OF YMAX, NTOT, AND NZERO ARE ABSOLUTELY NECESSARY FOR THE
DETERMINATION OF THE Y-AXIS IN THE PLOT. YMAX IS REQUIRED TO EQUAL ZERO
(YMAX=0.), IN ORDER FOR THE NEW AUTOSCALING CARD TO BE PUNCHED.

TWO PARAMETER CARDS ARE NECESSARY FOR EACH SPECTRA TO BE NORMALIZED
AND PLOTTED.

CARD 1: N, NO, NDLY, OVF, CG, VELOC, NOPT, FLAG
(3I5,3F10.5,2I5)

CARD 2: TEXT(I), I=1,9
(9A8)

THE ABOVE IS CARD SET 1

IF THE USER WISHES TO USE THE REPLOT OPTION, HE SHOULD USE CARD SET 2 OF
CARD SET 3.

CARD 3: (BLANK CARD)

CARD 4: TITLE CARD (SAME AS CARD 2)

CARD 5: AUTOSCALING CARD (YMAX, YMIN, CG, VELOC, NTOT, NZERO, FLAG)
(3F10.5,2F10.8,3I5)

* NORMALIZED DATA DECK *

THE ABOVE IS CARD SET 2.

NOTE: AUTOSCALING CARD WAS FOUND WITH THE TITLE CARD AND THE NORMALIZED
DATA DECK.

IF AUTOSCALING CARD IS NOT FOUND WITH THE TITLE CARD AND NORMALIZED DATA
DECK, THEN CARD 5 IS REPLACED WITH CARD 6.

CARD 3
CARD 4

CARD 6: PARTIAL AUTOSCALING CARD (0..0..0..0..NTOT, NZERO, FLAG)
(3F10.5,2F10.8,3I5)

* NORMALIZED DATA DECK *

THE ABOVE IS CARD SET 3.

ADDITIONAL ARRAYS AND PARAMETERS USED

IDAT(1200)=ARRAY OF INITIAL RAW DATA.
ROAT(1200)=ARRAY OF NORMALIZED DATA.
ARRAY(9)=ARRAY USED TO TRANSMIT LABELS FOR PLOTS.
NZERO=NO+NDLY, THE NUMBER OF POINTS AT THE BEGINNING
WHICH ARE SET TO ZERO.
ADD=OVF*1048578, THE NUMBER OF COUNTS TO BE ADDED TO
THE RAW DATA FOR OVERFLOWS.
FACT=NORMALIZING FACTOR OBTAINED BY AVERAGING 5 POINTS
AT EACH OF THE OUTER EXTREMES OF THE SPECTRA AND
SETTING THAT TO 100.
YMAX=LARGEST VALUE OF RDAT.
YMIN=SMALLEST VALUE OF RDAT.

OUTPUT: THE FOLLOWING IS CONTAINED ON THE OUTPUT UNITS.

PUNCH:
1) LABEL CARD WITH TEXT(1) AS A LABEL.
2) TITLE CARD WITH TEXT(I) ON IT.
3) PARAMETER AND AUTOSCALING CARD CONTAINING
   YMAX, YMIN, CG, VELOC, NTOT, NZERO, FLAG
(3F10.5,2F10.8,3I5)
4) THE NORMALIZED DATA AND CORRESPONDING CHANNEL NUMBER.
LINEPRINTER:
1) TEXT(I) AT TOP OF PAGE AS TITLE.
2) CONSTANTS OF CALCULATION
   \( N, NO, NOLY, OV, CG, VELC, TEXT(1), FLAG \).
3) THE RAW EXPERIMENTAL DATA WITH OVERFLOWS ADDED IN AND
   THE CORRESPONDING CHANNEL NUMBER.
4) THE TITLE AT THE TOP OF A NEW PAGE.
5) AUTOSCALING INFORMATION \( (YM, YM, NTOT, NZERO, FLAG) \)
   6) NORMALIZED DATA \( (I, ROAT(I), I=1, NTOT) \)
   \( (1X, 6(I4, F8.3)) \)

PLOTTER:
1) TITLE OF THE PLOT.
2) DATA PLOTTED WITH SMALL CIRCLES AS DATA POINTS.
3) LABELED ABCISSA WITH THE FIRST NON-ZERO DATAPOINT
   LABELED AND THE LAST DATA POINT LABELED AND TIC-MARKS
   AT EVERY 10 CHANNELS. THE ORDIATE IS LABELED WITH
   LARGE TIC-MARKS AT EVERY UNIT AND SMALL TIC-MARKS
   AT HALF-INTEGER POINTS.
4) IF VELC AND CG ARE NON-ZERO, AN ADDITIONAL ABCISSA
   IS ADDED WITH VELOCITY IN MM/SEC AS THE UNITS.
   CG AND VELC ARE ALSO WRITTEN OUT AT THE TOP IF
   THEY ARE NON-ZERO.
5) IF NOPT IS NON-ZERO A SEPARATE PLOT OF INTENSITY
   VS VELOCITY IS PLOTTED ON A SCALE OF 1MM/SEC=.5 INCH.
6) IF FLAG IS ONE BACKGROUND CORRECTION STATEMENT PRINTED
   7) SCALING ON THE PLOT GIVES AN ORDIATE OF 7.57 INCHES
      AND AN ABCISSA OF 8.95 INCHES.

TO CREATE AND RUN THE BINARY DECK, NOTING THAT THE SYMBOL *** IS
USED TO DENOTE THE CONTROL MODE SYMBOL, OR THE 7/8 ON THE CARDS.

FROM TELETYPE (DECKNAME OF MOSSRED IS ASSUMED)

```
?FORTRAN,I=MOSSRED,0,E,X
```

THE X OPTION CREATES THE BINARY ON LUN 56, TO SAVE THE BINARY
USE: (NOTE, P OPTION IN FORTRAN WILL ALSO PUNCH THIS DECK)
```
?SAVE,56=MOSSRED9
```

TO CREATE A PUNCHED DECK, USE: (UNLESS OTHERWISE EQUIPPED.
LUN 62=PUN)
```
?LABEL,62/SMITH (OR WHATEVER NAME YOU WANT)
```
```
?COPY,I=MOSSRED9,0=62
```

TO RUN THE DECK JUST CREATED, FROM BATCH, USE THE FOLLOWING DECK:
```
?JOB ............
?EQUIP,10=PLOT
?EQUIP,15=LP
?EQUIP,16=PUN
?LABEL,10/SAVE FOR SMITH
?LABEL,15/SAVE FOR SMITH
?LABEL,16/SMITH
?FORMS,10/PT-05 PLEASE (LIMIT OF 7 CHARACTERS ON PUNCH LABEL)
?TIME = 200 (GIVES ENOUGH TIME TO RUN)
?MF3LKS = 400 (GIVES YOU ENOUGH FILE SPACE FOR RUN
EACH SPECTRA REQUIRES ABOUT .40 FILE
```
READ IN INITIAL PARAMETERS AND TEST EXIT CRITERIA (N>1200)

90    READ 100, N, NC, NDLY, OVFC, VELC, NOPT, FLAG
100   FORMAT (3I5, 3F10.5, 2I5)
      IF (N.GT.1200) CALL EXIT
      IF (N.EQ.01 GO TO 950
      READ 110, (TEXT(I), I=1, 9)
110   FORMAT (9A4)

CALL LABELP (16, TEXT(1))
CALL EQUIP (20, TEXT)
WRITE (15, 130) (TEXT(I), I=1, 9)
WRITE (16, 135) (TEXT(I), I=1, 9)
OS3 FORTRAN VERSION 3.13 MOSSRED 02/12/78 1659

130 FORMAT (1H1,9A8)
135 FORMAT (9A9)
C READ IN IDAT ARRAY.
C 140 READ(20,120) (IDAT(I),I=1,N)
120 FORMAT (9(I6,1X),I6)
C WRITE OUT CONSTANTS OF CALCULATION AND HEADINGS ON LINE PRINTER.
C 140 FORMAT (15,140) N,NOLY,OVF,VELC,TEXT(1)
140 FORMAT (1H0.26X,(1CHA COUNT ),/)  
C CHECK FOR BACKGROUND SLOPE FLAG.
C 145 WRITE (15,150)
150 FORMAT (1H0.26X,(1CH COUNT ),/)  
C IF (FLAG.NE.1) GOTO 145
C 146 FORMAT (5X,5X*BACKGROUND SLOPE CORRECTED*)
C WRITE (15,160)
160 FORMAT (1H0.26X,(1CHA COUNT ),/)  
C ADD OVERFLOWS AND PRINT OUT EXPERIMENTAL RESULTS
C 170 ROAT(K)=IDAT(I)+ADD
DO 180 I=1,NZERO
180 ROAT(I)=0.0
WRITE (15,190) (J,ROAT(J),J=1,NTOT)
190 FORMAT (1H0.26X,(1CHA COUNT ),/)  
C DETERMINES NORMALIZING FACTOR.
C 200 AVG1=AVG2=0.0
N1=NZERO+3
N2=NZERO+7
N3=NTOT+7
N4=NTOT+3
DO 200 K=N1+N2
200 AVG1=AVG1+ROAT(K)
DO 210 K=N3+N4
210 AVG2=AVG2+ROAT(K)
C CHECK FOR CORRECTION OF BACKGROUND SLOPE FLAG.
IF (FLAG.NE.1) GOTO 215
CALL 3KGCOR(ROAT,NTOT,AVG1,AVG2,NZERC1)

NORMALIZATION OF SPECTRUM.

DETERMINATION OF YMAX AND YMIN.

YMIN=100.,
YMAX=100.,
FACT=1000./(AVG1+AVG2)
DO 220 I=NZERO1,NTOT
   ROAT(I)=ROAT(I)*FACT
   IF(RDAT(I) .GT. YMAX) YMAX=RDAT(I)
   IF (ROAT(I) .LT. YMIN) YMIN=ROAT(I)

PRINT HEADINGS AND SCALING FACTORS ON LP.

WRITE (15,130) (TEXT(I),I=1,9)
WRITE (15,248) YMAX,YMIN,NTOT,NZERO
WRITE (15,230)

PRINT AND PUNCH NORMALIZED SPECTRUM.

WRITE (15,251) (I,ROAT(I),I=1,NTOT)
WRITE (16,250) (I,ROAT(I),I=1,NTOT)

THIS OPTION (IF N=0) ALLOWS THE USER TO RE- PLOT A SPECTRA, READING
THE DECK FROM CARDS GENERATED BY THIS PROGRAM.

READ 135,(TEXT(I),I=1,9)
READ 245,YMAX,YMIN,CG,VELC,NTOT,NZERO,FLAG
READ 250,(I,ROAT(I),I=1,NTOT)
NZERO1 = NZERO + 1
CONTINUE

IF AUTOSCALING CARD IS NOT PRESENT THIS OPTION WILL PUNCH ONE.
IF (YMAX .NE. 0.) GO TO 866
YMAX = YMIN = 100.
DO 365 I=NZERO+1,NTOT
     IF (ROAT(I).GT.YMAX) YMAX = ROAT(I)
365 IF (RDAT(I).LT.YMIN) YMIN = RDAT(I)
WRITE(16,245) YMAX,YMIN,CG,VELC,NTOT,NZERO,FLAG
CALL LABELP (16,TEXT(1))

C BEGIN PLOTTING SEQUENCE.
C PLOT INTENSITY VS CHANNEL NUMBER
C
866 CALL VECTORS

C DRAW BOX AROUND PLOT FOR CUTTING PURPOSES.
C
CALL SIZE (27.9,10.)
CALL SCALE (1..1,.0..0..0..0.)
CALL PLOT (10..0..0..0.)
CALL PLOT (11..0..1..0)
CALL PLOT (11..8.5..1,0)
CALL PLOT (10..8.5..1,0)
CALL PLOT (0..0..1..0)
CALL POINTS
CALL PLOT (1.25,8.2,1.28)
CALL PLOT (5.50,8.2,1.28)
CALL PLOT (9.75,8.2,1.28)
CALL SYMBOL (4.3,8.55,0..12.70,CUTOUT)
CALL VECTORS

C SET UP SCALING OF PLOT
C
XMAX=NTOT
XMIN=NZERO1
X0IF=XMAX-XMIN
Y0IF=YMAX-YMIN
YMIN=YMIN-(.50*YOIF)
YMAX=YMAX+(.50*YOIF)
YOIF=YOIF*2.0

C DEFINE PHYSICAL BOUNDARIES
C
XSCAL=8.5455/X0IF
YSCAL=6.5636/Y0IF
CALL SCALE (XSCAL,YSCAL,1.5,1.,XMIN,YMIN)

C DISPLACE PENT FOR DRAWING CAPTIONS
C
X0DIS=.24/XSCAL
Y0DIS=.64/YSCAL
X0DIS=.24/YSCAL
Y0DIS=.38/YSCAL

C DRAW AND LABEL X-AXIS
C
ENCOD (3,310,ARRAY) XMIN
FORMAT(F3.0)
CALL SYMBOL (XMIN=XXDIS,YMIN=Y0DIS,0.,16,3,ARRAY)
CALL PLOT (XMIN,YMIN,0.,0.)
CALL PLOT (XMIN,YMIN,1.,0)
XMAX=XMAX/NZER01/10
OS3 FORTRAN VERSION 3.13 MOSSRED 02/12/78 1659

320 XP=XP+10.
   IF (XP .GE. XMAX) GO TO 330
   CALL PLOT (XP, YMIN+1.8)
   GO TO 320

330 CALL PLOT (XMAX, YMIN+1.8)
   ENCODE (3, 310, ARRAY) XMAX
   CALL SYMBOL (XMAX-XDIS, YMIN-YDIS, 0...16, 3, ARRAY)
   CALL PLOT (XMIN, YMIN, 0, 0)

C
C DRAW Y-AXIS
C
   YP=YP+10.
   YLMK=YP+1.
   YHMK=YP+1.
   IF (YP .GE. YMAX) GO TO 330
   CALL PLOT (XMIN, YP, 1, 5)

340 CALL PLOT (XMIN, YP, 1, 5)

350 CALL PLOT (XMIN, YP, 1, 6)
   YP=YP+.5
   IF (YP .LT. YHMK) GO TO 340
   IF (YP .GE. YMAX) GO TO 360
   CALL PLOT (XMIN, YP, 1, 5)

360 CALL PLOT (XMIN, YMAX, 1, 4)

C
C LABEL Y-AXIS
C
   ENCODE (3, 310, ARRAY) YLMK
   CALL SYMBOL (XMIN-XDIS, YLMK-YDIS, 0...16, 3, ARRAY)
   ENCODE (3, 310, ARRAY) YHMK
   CALL SYMBOL (XMIN-XDIS, YHMK-YDIS, 0...16, 3, ARRAY)

C
C LABEL PLOT WITH TITLE
C
   ENCODE (72, 110, ARRAY) (TEXT(I), I=1, 9)
   CALL SYMBOL (XMIN, YMAX, 0...12, 72, ARRAY)

C
C CHECK FOR BACKGROUND SLOPE FLAG.
C
   IF (FLAG .NE. 1) GOTO 365
   CALL SYMBOL (XMIN, YMAX+2*3/YSCAL), 0...12, 25, BCKGRN

365 CALL POINTS

C
C PLOT DATA
C
   DO 370 I=1, NTOT
   FI=I
   370 CALL PLOT (FI, RDATA(I), 1, 27)

C
C CALL VECTORS
C
   IF (CG .EQ. 0.0) GO TO 600

C
C WRITE OUT CENTER OF GRAVITY AND CALIBRATION CONSTANT ON PLOT IF
C CG IS NON-ZERO.
C
   ENCODE (65, 700, ARRAY) VELC, CG
   IF (CG .NE. 0.0) FORMAT (4X, CAL CONST = *.F10.7, 2 MM/SEC/CH, 5X, CG = *.F10.4, 1X, CHANNELS*)
This code generates the velocity axis on the data plot. If CG is non-zero, for this section, the following parameters are important:

- \( \text{VELMIN} = \text{MINIMUM in velocity corresponding to } X_{\text{MIN}} \)
- \( \text{VELMAX} = \text{MAXIMUM in velocity corresponding to } X_{\text{MAX}} \)
- \( \text{VAX} = \text{OFFSET of velocity axis above channel axis} \)
- \( \text{VLMK} = \text{Low value on vel axis to be labeled} \)
- \( \text{VHMK} = \text{High value on vel axis to be labeled} \)

Set up initial parameters required:

\[
\begin{align*}
\text{VELMIN} &= (X_{\text{MIN}} + \text{CG}) \times \text{VELC} \\
\text{VELMAX} &= (X_{\text{MAX}} + \text{CG}) \times \text{VELC} \\
\text{VEL1} &= 1 \times \text{VELC} \\
\text{VLMK} &= \text{IVL} = \text{VELMIN} \\
\text{DEL} &= \text{VLMK} - \text{VELMIN} \\
\text{VAX} &= 0.5 \times \text{YSCL} + Y_{\text{MIN}} \\
\text{VHMK} &= \text{IVH} = \text{VELMAX}
\end{align*}
\]

Draw velocity axis.

\[
\begin{align*}
\text{CALL PLOT}(X_{\text{MIN}}, V_{\text{AX}}, 0, 0) \\
V_{\text{POS}} &= X_{\text{MIN}} + \text{DEL} \times \text{VELC} \\
600 \quad \text{CALL PLOT}(V_{\text{POS}}, V_{\text{AX}}, 1, 8) \\
V_{\text{POS}} &= V_{\text{POS}} + \text{VEL1} \\
\text{IF} \ (V_{\text{POS}} \leq X_{\text{MAX}}) \ \text{GO TO 800} \\
\text{CALL PLOT}(X_{\text{MAX}}, V_{\text{AX}}, 1, 0)
\end{align*}
\]

Label velocity axis at VLMK, 0, and VHMK:

\[
\begin{align*}
V_{\text{POS}} &= CG - 0.04 \times \text{XSCL} \\
\text{CALL SYMBOL}(V_{\text{POS}}, V_{\text{AX}} - Y_{\text{DIS}}, 0...16, 1, 10) \\
V_{\text{POS}} &= CG + \text{VLMK} \times \text{VEL1} \\
\text{ENCODE (3, 326, ARRAY)} \ \text{IVL}
\end{align*}
\]

Format (13):

\[
\begin{align*}
\text{CALL SYMBOL}(V_{\text{POS}} - 0.2 \times \text{XSCL}, V_{\text{AX}} - Y_{\text{DIS}}, 0...16, 3, \text{ARRAY}) \\
V_{\text{POS}} &= CG + \text{VHMK} \times \text{VEL1} \\
\text{ENCODE (3, 326, ARRAY)} \ \text{IVH} \\
\text{CALL SYMBOL}(V_{\text{POS}} - 0.32 \times \text{XSCL}, V_{\text{AX}} - Y_{\text{DIS}}, 0...16, 3, \text{ARRAY})
\end{align*}
\]

Draw vertical line at \( VEL = 0 \).

\[
\begin{align*}
\text{CALL PLOT}(CG, 100, 0, 0) \\
\text{CALL PLOT}(CG, V_{\text{AX}}, 1, 0) \\
\text{IF} \ (\text{NOPT}) \ \text{GO TO 601, 600}
\end{align*}
\]

This part of the code draws the plot of intensity vs velocity with the velocity axis calibrated with 1mm/sec = .5 inches.

Begin by establishing the constants for Complot.

\[
\begin{align*}
\text{XDIS} &= 0.32 \times \text{XSCL} \\
\text{YDIS} &= 0.16 \times \text{YSCL}
\end{align*}
\]

Label velocity axis.
C
ENCODE (4,380,ARRAY) VLMK
380 FORMAT (F1.1)
CALL SYMBOL (VLMK-XXDIS,YMIN-YXDIS,0..16,4,ARRAY)
ENCODE (4,380,ARRAY) VHMK
CALL SYMBOL (VHMK-XXDIS,YMIN-YXDIS,0..16,4,ARRAY)
CALL PLOT (VELMIN,YMIN,0,0)
VPOS = VLMK
870 CALL PLOT (VPOS,YMIN,1,0)
VPOS = VPOS + 1.
IF (VPOS.LE.VELMAX) GO TO 870
CALL PLOT (VELMAX,YMIN,1,0)
C
C
DRAW Y-AXIS.
C
CALL PLOT (0.0,YMIN,0,0)
YP=1YP
YP=YP+.5
IF (YP.NE.IYP) GO TO 410
400 CALL PLOT (0.0,YP,1,5)
410 YP=YP+.5
CALL PLOT (0.0,YP,1,6)
YP=YP+.5
IF (YP.LT.YHMK) GO TO 400
IF (YP.GE.YMAX) GO TO 420
C
CALL PLOT (0.0,YP,1,5)
420 CALL PLOT (0.0,YMAX,1,0)
C
C
LABEL Y-AXIS.
C
ENCODE (3,310,ARRAY) YLMK
CALL SYMBOL (-XXDIS,YLMK-YYDIS,0..16,3,ARRAY)
ENCODE (3,310,ARRAY) YHMK
CALL SYMBOL (-XXDIS,YHMK-YYDIS,0..16,3,ARRAY)
ENCODE (72,110,ARRAY) (TEXT(I),I=1,9)
CALL SYMBOL (VELMIN,YMAX,0..12,72,ARRAY)
C
C
DRAW DATA POINTS WITH SMALL CIRCLES AS DATA MARKS.
C
VPOS = VELMIN
CALL POINTS
DO 430 I=NZERO1,NTOT
CALL PLOT (VPOS,ROAT(I),1,27)
430 VPOS = VPOS +VELC
600 CALL PLOTEND
CALL UNEQUP (20)
ENDFILE 16
GO TO 90
END
SU3ROUTINE 3KGCOR(ROAT,NTOT,AVG1,AVG2,NZERO1)

C PROGRAM TO CORRECT THE BACKGROUND OF A MOSSBAUER SPECTRA
C FOR SLOPE IN THE BACKGROUND BY A RATIO METHOD
C
DIMENSION ROAT(1200)

C
AVE1= AVG1/5.
AVE2= AVG2/5.
DEL=AVE2-AVE1
DELT = AVE2 * (NTOT-9-NZERO1)
DELT = DEL/DELT
DO 60 I=NZERO1,NTOT
ROAT(I)=ROAT(I)*(1.-I-1)*DELT)
60 CONTINUE

AVG2=AVG1
RETURN
END
PROGRAM SWMPLOT
C SWMPLOT GENERATES A SERIES OF PLOTS IN COLUMN FASHION BY STACKING
C THE PLOTS UP TO 15 PLOTS HIGH. THE PROGRAM ALLOWS THE USER TO
C PLOT ANY COMBINATION OF THE FOLLOWING.
C
1.) DATA IN THE FORMAT OF X, THEN Y (6(F4.0,F8.3))
2.) LORENTZIAN MODEL 1
3.) LORENTZIAN MODEL 2
4.) HYPERFINE MODEL CALCULATED FROM H(EFF),E**2*Q*Q,...
4a.) THEORETICAL SPECTRA OF USER FORMATED TYPE. (MUST BE X,Y DATA)
C THE ORDER OF OPERATION OF THE PROGRAM IS AS FOLLOWS:
C
1. INITIALIZE PLOTTING (DRAW X AXIS)
2. PLOT DATA
3. DRAW Y AXIS
4. PLOT LORENTZIAN MODEL 1
5. PLOT LORENTZIAN MODEL 2
6. PLOT HYPERFINE MODEL
7. PLOT THEORETICAL SPECTRA
8. ADVANCE TO NEW PLOTTING REGION AND RETURN TO STEP 2
C
TO INITIALIZE THE PROGRAM THE USER MUST PROVIDE THE FOLLOWING
NCOL = NUMBER OF COLUMNS OF PLOTS (MAX OF 2)
NPLTS = NUMBER OF PLOTS PER COLUMN (MAX OF 15)
NTYPE = PLOTTING CHOICE PARAMETER. IF NTYPE=0, THE
CALCOMP PLOTTER IS USED. IF NTYPE = 3, THE SMALL
GERBER PLOTTER IS USED.
XSIZE = LENGTH OF X AXIS IN INCHES (DEFAULT = 10.
YSIZE = LENGTH OF Y AXIS IN INCHES (DEFAULT = 4.)
CHARSZ = SIZE OF CHARACTERS IN LABELS (DEFAULT = .32)
BIASF = SPACING BETWEEN TOP OF ONE PLOT AND BOTTOM OF NEXT.
XLOW = LOW VALUE OF X AL 0WED
XHIGH = HIGH VALUE OF X ALLOWED
XINC = INCREMENT FOR TICS ON X AXIS (STARTING FROM ZERO)
NLBL = LABELING FREQUENCY. IF NLBL = 1, EVERY TIC IS LABELED
IF NLBL=2 EVERY OTHER TIC IS LABELED STARTING AT 0.......
FMT = FORMAT OF THE THEORETICAL SPECTRA
(EG.(6(F4.0,F8.3)))
C OPTIONS AND OPTION FLAGS
IF ANY OF THE OPTION PARAMETERS ARE NON-ZERO THE OPTION
IS INITIATED AND THE CARDS NECESSARY FOR THAT OPTION
WILL BE READ
C OPTION FLAGS
NOAT CALLS SUBROUTINE DATPLOT
NLREN1 CALLS SUBROUTINE PNLREN1
NLREN2 CALLS SUBROUTINE PNLREN2
NHEFF CALLS SUBROUTINE P2
NTH CALLS SUBROUTINE PLOTTH
C T CALLS SUBROUTINE TANDM WHICH PRINTS OUT THE
C VALUE OF T ON THE PLOT
C
C EACH OF THE ABOVE SUBROUTINES READS INPUT CARDS. THESE CARDS
C EXPLAINED IN THE VARIOUS SUBROUTINES. THE Routines ARE CALLED
C IN THE ORDER THAT THEY ARE LISTED ABOVE, AND THEREFORE THE CARDS
C TO BE READ BY THE ROUTINES MUST BE IN THAT ORDER. OBVIOUSLY IF
C A ROUTINE IS NOT CALLED INPUT CARDS FOR THAT OPTION ARE NOT
C NECESSARY.
THE FOLLOWING INPUT CARDS ARE NECESSARY TO RUN THE PROGRAM.
IF ANY OPTIONS ARE USED THE INPUT PARAMETERS ARE LISTED IN THE
SUBROUTINE FOR THAT OPTION.

***INPUT CARDS***

CARD 1 (3I5)

COLUMN
 1  5  NCOL
 5 10  NPLTS
11 15 NTYPE

CARD 2 (4F10.5)

COLUMN
 1  9  XSIZE (LEAVE BLANK FOR DEFAULT)
11 20  YSIZE (DITTO)
21 30  CHARSZ (DITTO)
31 40  3IASF (DITTO)

CARD 3 (3F10.5, I5)

COLUMN
 1  9  XLOW
11 20  XHIGH
21 30  XINC
31 35  NLBL

CARD 4 (10A8)

COLUMN
 1  80  FMT

CARD 5 (5I5,F5.0)

COLUMN
 1  5  NDAT
 6 10  NLEN1
11 15  NLEN2
16 20  NHEFF
21 25  NTH
26 30  T

***RUNNING THE PROGRAM***

THIS ASSUMES THAT THE PROGRAM IS BEING RUN ON OS-3 AND THAT A
BINARY FILE OF THIS PROGRAM EXISTS AND IS CALLED BINFILE.
THE CONTROL MODE SYMBOL # WILL DENOTE THE 7/8 PUNCH ON A
CARD.

?JOB, ******
?EQUIP, 10=PLOT
?LABEL +10/SAVE FOR SMITH (OR WHATEVER NAME YOU CHOSE)
?FORMS +10/PT=05 PLEASE (IF YOU WANT A SPECIAL PEN ON PLOTTER)
?MFILKS = 400
?TIME = 200
?LOAD BINFILE,L=*COMPLET
RUN
CARD 1
CARD 2
CARD 3
CARD 4
CARD 5

DECKS OR CARDS AS REQUIRED BY OPTIONS SPECIFIED ON ABOVE
CARD TYPE 5

DECK FOR OPTIONS ON SECOND PLOT FROM CARD TYPE 5

THIS IS REPEATED UNTIL ALL PLOTS ARE DONE.
WHICH IS NCOL * NPLTS TIMES THAT CARD TYPE 5 FOLLOWED BY
THE NECESSARY DECK IS USED.

LOGOFF

******************************************************************************

***ACTION TAKEN BY THIS ROUTINE (OUTPUT)***

***PLOTTER OUTPUT***

1. DRAW THE X AXIS. XSIZE INCHES LONG.
2. PLACE TIC MARKS ON THE X AXIS STARTING FROM ZERO AT
   INTERVALS OF XINC.
3. LABEL THE APPROPRIATE TIC MARKS. STARTING FROM ZERO,
   SKIPPING NLBL - 1 TIC MARKS AND LABELING THE NEXT TIC MARK,
   UNTIL THE X AXIS HAS BEEN LABELED IN BOTH DIRECTIONS.
4. IF NO LABELS ARE DESIRED, NLBL SHOULD BE SET TO A NUMBER
   GREATER THAN THE AVAILABLE NUMBER OF TIC MARKS. THIS IS
   DUE TO THE FACT THAT THE LABELING OF THE AXIS AND DRAWING
   THE AXIS WITH TIC MARKS IS DONE AT THE SAME TIME.
   STARTING AT ZERO, THE AXIS IS DRAWN BY DRAWING THE TIC MARK
   AND CONNECTING IT WITH THE PREVIOUS MARK. THE PROGRAM
   COUNTS OVER NLBL TIC MARKS AND LABELS THAT TIC MARK. IT
   THEN COUNTS OVER NLBL MORE TIC MARKS AND DRAW THEM
   AND LABELS THE APPROPRIATE ONE. THIS CONTINUES UNTIL
   THE AXIS HAS BEEN DRAWN AND LABELED IN BOTH DIRECTIONS.
   IF THE PROGRAM REACHES EITHER XHIGH OR XLOW BEFORE
   COUNTING NLBL TIC MARKS, NONE ARE LABELED.
5. AT HE END OF THE ROUTINE, THE X AXIS WILL BE LABELED
   VELOCITY (CM/SEC)* AND THE Y AXIS WILL BE LABELED
   RELATIVE TRANSMISSION*.

******************************************************************************

***SOME ADDITIONAL COMMENTS***

1. IF ALL OPTION FLAGS ARE ZERO A BLANK IS LEFT IN THE COLUMN
   FOR THAT PLOT
2. PLOTTING ORDER HAS THE PROGRAM STARTING WITH THE LEFT MOST
COLUMN AND THE BOTTOM PLOT. THE PLOTS ARE DONE SUCH THAT
THE FIRST COLUMN IS COMPLETED, THEN THE SECOND COLUMN IS
STARTED.

3. FOR EVERY PLOT, A REGION XSIZE BY YSIZ IS DEFINED. THE
DISTANCE BIASF IS SUBTRACTED FROM YSIZ TO DETERMINE THE
PHYSICAL HEIGHT OF THE PLOT. THE BLANK AREA BIASF INCHES
WIDE IS LEFT AT THE BOTTOM OF THE PLOT. (EG. IF YSIZ=4,,
AND BIASF=.1, THE TOTAL HEIGHT ALLOWED FOR EACH PLOT
WOULD BE 4 INCHES BUT THERE WOULD BE 1 INCH BLANK AT
THE BOTTOM AND THE PLOT WOULD ONLY OCCUPY 3 INCHES ABOVE
THE BLANK AREA.)

**************END OF COMMENT FIELD**********************

DIMENSION 3DARRAY(10)
DIMENSION REL(3),FMT(10),VEL(3)
DATA (REL = 21RELATIVE TRANSMISSION)
DATA (VEL=17VEL OCITY (CH/SEC))
COMMON/ONE/XLOW,XHIGH,SIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
10 FORMAT (515.F5.0)
15 FORMAT(4F10.5)
20 FORMAT (3F10.0,15)
30 FORMAT(10A)

C
C OFFX AND OFFY ARE OFFSETS IN THE X AND Y DIRECTIONS FOR THE PLOTS
C
OFFX=.2.
OFFY=.2.

C READ IN THE INPUT CARDS TO DEFINE THE PLOT
C
READ 10,NCOL,NPLTS,NTYPE
READ 15,XSIZE,YSIZ,CHARSZ,BIASF
READ 20,XLOW,XHIGH,XINC,NLBL
READ 30,FMT

C CHECK PARAMETERS FOR SIZE AND SET TO DEFAULT VALUES IF ZERO
C
IF(BIASF.EQ.0.) BIASF = .2
IF(YSIZ.EQ.0.) YSIZ=4.
IF(XSIZE.EQ.0.) XSIZE = 10.
IF(CHARSZ.EQ.0.) CHARSZ=.32

C REDEFINE BIASF IN TERMS OF THE FRACTION OF THE PLOT
C REGION (YSIZ HIGH) THE ACTUAL PLOT WILL OCCUPY.
C
BIASF = BIASF/YSIZ.
XSIZ = NCOL*(XSIZE + OFFX * 2.) - OFFX * 1.
DELX=XHIGH-XLOW
PLHT =NPLTS*YSIZ
XFACT=XSIZ/DELX
CALL PLOTTYPE(NTYPE)
CALL SIZE (XSIZ,PLHT+8.)

C OFFSET FOR DRAWING LABEL ON X AXIS
C
XXOFF = CHARSZ/(XFACT*2.)
YYOFF=1.5*CHARSZ

C OFFSET IN X DIRECTION FOR POSITIONING THE PHRASE \x = \ldots \x
C ON PLOT
C OFFSET IN X DIRECTION FOR TITLE OF PLOT
C XTOFF = XHIGH - (7.*CHARSZ/XFACT)
C
C OFFSET FOR WRITING A ZERO ON X AXIS
C ZXOFF = -CHARSZ/(4.*XFACT)
C
C SET UP OFFSETS FOR WRITING OUT 100 AND 99 ON DATA PLOTS
C
C CSIZN = CHARSZ * 2./3.,
XOFF99 = 2.5*CSIZN/XFACT
C
C START DRAWING THE X AXIS
C
C XOFF=OFFX
YOFF=OFFY
DO 100 M=1,NCOL
CALL SCALE(XFACT,1.,XOFF,YOFF,XLOW,0.)
XP=0.
XPT=XHIGH
C
C DRAW THE ZERO ON THE X AXIS
C
CALL SYMBOL(ZXOFF,-XYOFF,0.,CHARSZ,1,1H0)
C
C DRAW THE CENTER OR ZERO POINT ON X AXIS
C
CALL PLOT (0.,0.,0.,0)
CALL PLOT (0.,0..1,8)
C
C START LOOP TO DRAW THE POSITIVE THEN NEGATIVE SIDE OF THE X AXIS
C
DO 130 M2=1,2
IF (XINC.EQ.0.) GO TO 120
105 DO 110 M1=1,NCOL
XP=XP+XINC
IF(ABS(XP).GT.ABS(XPT)) GO TO 120
110 CALL PLOT (XP,0.,1,8)
CALL LABELS (XP,3CDARAY,NCHAR)
CALL SYMBOL(XP=XOFF*NCHAR,-XYOFF,0.,CHARSZ,NCHAR,BCDARAY)
CALL PLOT(XP,0.,0,9)
GO TO 105
120 CALL PLOT (XPT,0.,1,8)
CALL PLOT(9.,0.,0,9)
XP=0.
XINC=-XINC
130 XPT= XLOW
100 XOFF=XOFF+XSIZE+OFFX+OFFX
C
C START OF PLOTTING OF THE OPTIONS
C
C IFLAG IS FLAG WHICH IS ZERO IF P2 HAS NOT BEEN USED
C AND ONE IF P2 HAS BEEN USED
C
IFLAG = 0
XOFF=OFFX
DO 200 M=1,NCOL
DO 202 L=1,NPLTS
  H=H.
  SCAL = 0.
C READ OPTION CARD
C THE ALL IMPORTANT PARAMETER SCAL IS DESCRIBED IN SUBROUTINE
C DATPLOT
C
READ 10,NOAT,NLREN1,NLREN2,NHEFF,NTH,T
IF (NCFAT,NE,0) CALL DATPLOT(SCAL,M,L,XLOFF,CSIZ,YOFF)
CALL YAXIS(SCAL)
IF (NLREN1,NE,0) CALL PNREN1(SCAL,NLREN1,M,L)
IF (NLREN2,NE,0) CALL PNREN2(SCAL,NLREN2,M,L)
IF (NHEFF,NE,0) CALL P2H(SCAL,IFLAG,M,L)
IF (NTH,NE,0) CALL PLOTTH(SCAL,FMT,NTH)
IF (T,NE,0 OR,H,NE,0) CALL TANDH(SCAL,T,H,XTOFF)

202 YOFF=YOFF+YSIZ
YOFF=OFFY
200 XOFF=XOFF+XSIZE+OFFX+OFFX
XOFF=OFFX
C PRINT PHRASES #RELATIVE TRANSMISSION# AND #VELOCITY (CM/SEC)#
C ON PLOTS
C
DO 400 M=1,NCOL
  CALL SCALE(1,1,XOFF,YOFF,0,0,0)
  CALL SYMSOL(-OFFX/2,*(PLTHT-2,CHARSZ)/2.90.,
  1CHARSZ,21,REL)
  CALL SYMSOL((XSIZE-17,CHARSZ)/2.,-CHARSZ*4,0,CHARSZ,17,VEL)
400 XOFF=XOFF+XSIZE+OFFX+OFFX
CALL PLOTEND
END
SUBROUTINE DATPLOT(SCAL, M, L, XLOFF, CSIZN, XOFF99)
C
C this subroutine takes a data deck as produced by MOSSRED (Ver 3)
C and plots it on an axis in cm/sec. The data points are
C represented by small circles with a dot in the middle.
C
C******************************************************************************
C
C***INPUT PARAMETERS***
C
C TITLE = the title for the plot. The first 8 characters will
C be printed on the plot, and the whole title will be
C written on the line printer.
C
C YMAX = the maximum value of the data in relative transmission
C
C YMIN = the minimum value of the data
C
C CG = the centroid of an iron foil calibration used to
C calibrate this spectra. (in channels)
C
C CALCON = calibration constant for this spectra in mm/sec
C
C NPTS = the total number of data points
C
C NZERO = the number of data points with y = 0.
C these are expected to be at the beginning
C
C Y(i) = the data in relative transmission units, where
C the index i corresponds to the channel.
C
C this data above is punched out as part of the output of MOSSRED
C note that the CALCON is in mm/sec. This program converts it
C to cm/sec. If old data decks are used, some of the above
C information is not part of MOSSRED output. The user
C should check the data decks carefully to determine the
C presence of the autoscaling card (card containing first six
C parameters) and make sure it contains all the information.
C
C if no autoscaling card exists the user must make one. The
C YMAX and YMIN may be omitted from that card. As this program
C will calculate YMAX and YMIN if YMAX is omitted.
C
C******************************************************************************
C
C***INPUT CARDS FOR OPTION DATPLOT***
C
CARD I (10A8)
COLUMN
  1 - 80 TITLE

CARD 2 (4F10.5,2I5)
COLUMN
  1 - 10 YMAX
  11 - 20 YMIN
  21 - 30 CG
  31 - 40 CALCON
  41 - 45 NPTS
  46 - 50 NZERO

CARD 3 = A (6(4X,F8.3))
the data as provided by MOSSRED

******************************************************************************
COMMON/ONE/XLOW,XHIGH,BIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
COMMON/TWO/CALCON,CG,NL,XL,NH,XH,YMIN
DIMENSION Y(512)
DIMENSION TITLE(10)
C SCAL IS A VERY IMPORTANT PARAMETER TO THE SUCCESSFUL WORKING
C OF THIS PROGRAM, HOWEVER, ITS OPERATION IS LESS THAN OBVIOUS
C IT IS USED TO OBTAIN A PLEASANT LOOKING PLOT. IF A PLOT
C (THEORETICAL) IS TO BE OVERLAYED ON A DATA PLOT, THE
C PROBLEM ARISES AS TO WHERE TO PLACE THE BACKGROUND. SINCE
C THE BACKGROUND SCATTER WILL VARY FROM SPECTRA TO SPECTRA,
C THE AMOUNT OF PLOTTING REGION USED BY THE OTHER ROUTINES
C MUST VARY ACCORDINGLY, THIS IS THE PURPOSE OF SCAL.
C SINCE ALL MOSSBAUER SPECTRA HAVE A BACKGROUND APPROX. EQUAL
C TO 100. THIS IS THE REFERENCE POINT USED. THUS SCAL
C WILL BE THE HEIGHT IN INCHES FROM THE BACKGROUND REFERENCE
C POINT TO THE LOWEST VALUE IN THE PLOTTING REGION.
C THE REASON FOR THE REDEFINING OF THE MINIMUM VALUE HERE IS
C TO TAKE INTO ACCOUNT THE DISTANCE BIASF. IF MODIFICATIONS
C ARE PLANNED, CHECK THE CODE IN PLEN2 AS TO HOW SCAL AND
C BIASF ARE USED.
C IF SCAL IS SET TO 0, WHEN TAXIS IS CALLED, SCAL WILL
C EQUAL 90 PERCENT OF THE AVAILABLE PLOTTING REGION AS
C DEFINED IN THE MAIN PROGRAM UNDER ADDITIONAL COMMENTS.
C NUMBER 3.
C
SCAL=YFACT*(100.-YMIN)
IF(YMIN.GE.100. OR. YMAX.LT.100.) SCAL=0.
YMIN=YMAX=DELY
CALL SCALE(XFACT,YFACT,XOFF,YOFF,XLOW,YMIN)
CALCON = CALCON/10.
XL=(NZRO1-CG)*CALCON
XM=(NPTS-CG)*CALCON
XP=X=XL

C SEARCH FOR THE FIRST DATA POINT THAT IS IN THE PLOTTING REGION
C NL WILL BE THE INDEX OF THAT POINT AND XL WILL BE ITS RESPECTIVE
C VELOCITY.
C
DO 260 I=NZRO1,NPTS
NL=I
IF (XP.GE.XLOW) GO TO 270
260 XP=XP+CALCON
270 X=XL=XP
XP=XH

C SEARCH FOR THE LAST DATA POINT WITH VELOCITY LE XHIGH. NH CONTAINS
C THE INDEX FOR THAT POINT

DO 280 I=1,NPTS
   NH=I
   IF (XP.LE.XHIGH) GO TO 290
230   XP=XP+CALCON
290   NH=NPTS-NH+1
   CALL PLOT (X,Y(NL),0,0)

C PLOT THE DATA

CALL POINTS
DO 240 I=NL,NH
   CALL PLOT (X,Y(I),1,27)
240   X=X+CALCON
CALL VECTORS
CALL SYMBOL (XLOFF,YMIN+DELY/2.,0.,CHARSZ/2.,8.,TITLE(1))
IF(ISCAL.EQ.0.) RETURN
YOFF99 = CSIZN/(2.*YFACT)
CALL SYMBOL (XLOW-1.*XOFF99,100.,-YOFF99,0.,CSIZN,3,3H100)
IF(YMIN.LE.99.) CALL SYMBOL (XLOW-1.*XOFF99,100.,-YOFF99,10.,CSIZN,2,2H99)
RETURN
END
SUBROUTINE PNLREN1(SCAL,LREN,M,L)
C THIS SUBROUTINE PLOTS LORENTZIANS BASED ON THE MODEL OF MOSSFIT.
C THIS ROUTINE MUST BE USED WITH PLOTDAT, FOR IT OBTAINS SCALING,
C AND CALIBRATION CONSTANTS FROM THAT ROUTINE.
C
INPUT PARAMETERS

CARD 11 (F10.5)
COLUMN
1 - 10 9KG (ARBITRARY UNITS)

CARDS 2 - LREN + 11 (3F10.5)
COLUMN
1 - 10 MT
11 - 20 GAM (IN CHANNELS)
21 - 30 POS (IN CHANNELS)

DIMENSION HT(15),GAM(15),POS(15)
COMMON/ONE/XLOW,XHIGH,BIASF,XSIZE,YSIZE,CHARSZ,XOFF,YOFF,XFACT
COMMON/TWO/CALCONICG,NL,NHL,XH,YMIN
20 FORMAT (3F10.5)
91 FORMAT (*-FOR PLOT #,I3,* COLUMN #,I3,/,9X,#LREN#,15X,#AREA#)
92 FORMAT (10X,12,9X,E18.10)
PI2 = 2*ATAN(1.)
PRINT 91,L+M
READ 20, BKG
READ 20, MT, GAM, POS
GAM(K)=GAM(K)*CALCON
AREA=PI2*GAM(K)*HT(K)
GAM(K)=(GAM(K)/2.)**2
GAM(K)=1./GAM(K)
POS(K)=(POS(K)-CG)*CALCON
PRINT 92,K,AREA
X=XL
YCALC=9KG-YLREN(LREN,HT,GAM,POS,X)
CALL PLOT(X,YCALC,0,0)
DO 520 K1=NL,NH
CALL PLOT(X,YCALC,1,0)
Y=X+CALCON
520 YCALC=9KG-YLREN(LREN,HT,GAM,POS,X)
DO 530 K2=1,LREN
CALL PLOT(POS(K2),9KG,0,0)
CALL PLOT(POS(K2),9KG,1,6)
530 CALL PLOT(POS(K2),9KG-HT(K2),1,6)
RETURN
END
SUBROUTINE PNLREN2(SCAL,LREN,M,L)

C THIS SUBROUTINE PLOTS A THEORETICAL SPECTRA AS FROM
C INFORMATION PUNCHED OUT BY THE PROGRAM LUCK (DR. J. M. GROW).
C LUCK WILL PUNCH A DECK THAT WILL CONTAIN EITHER 32 OR 96 CARDS
C FOR SINGLE CRYSTAL OR POLYCRYSTALLINE SPECTRA RESPECTIVELY.
C EACH CARD CONTAINS THE HEIGHT, POSITION AND HALF-WIDTH AT HALF
C MAXIMUM FOR ONE LORENTZIAN.
C
C MODEL USED:
C 1.) LET 9KG = AN ARBITRARY BACKGROUND (IN THIS CASE, 100.)
C 2.) LET THE TERM (SUM(I))(F(I)) INDICATE THE SUM OVER ALL F
C BASED ON THE INDEX I.
C 3.) LET VEL(I) BE THE VELOCITY IN CM/SEC OF THE DATA POINT I
C 4.) LET OMEGA(I,J) = VEL(I) - POS(J)
C 5.) THEN WE HAVE FOR OUR MODEL
C
F(I) = 9KG - (SUM(J))(HT(J)*GAM(J)/(OMEGA(I,J)**2+GAM(J)**2)
C
NOTE THAT THIS MODEL IS NOT RESTRICTED TO ONLY THE OUTPUT FROM
LUCK BUT CAN BE USED BY ANY SYSTEM USING THIS MODEL
C
C***INPUT PARAMETERS***
C
LREN = NUMBER OF LORENTZIANS TO BE SUMMED OVER. THIS WILL BE
EITHER 32 OR 96. THIS IS SPECIFIED ON THE OPTION CARD AS
DELE = THE ISOMER SHIFT FOR THE SPECTRA. LUCK HAS NO PROVISION
FOR ISOMER SHIFT SO IT IS ADDED HERE.
NPTS = THE NUMBER OF POINTS TO BE PLOTTED (MAX OF 512)
HT(I) = THE HEIGHT OF THE PEAK
POS(I) = THE POSITION OF THE PEAK IN CM/SEC
GAM(I) = THE HALF-WIDTH AT HALF MAXIMUM OF THE PEAK IN CM/SEC

C***INPUT CARDS***
C
CARD 1 (F10.5,I5)
COLUMN
1 - 10 DELE
11 - 15 NPTS
C
CARDS 2 - LREN + 1 (3F10.5)
COLUMN
1 - 10 HT(I)
11 - 20 POS(I)
21 - 30 GAM(I)
C
DIMENSION HT(96),GAM(96),POS(96)
DIMENSION VEL(512),SPEC(512)
COMMON/XLOW,XHIGH,BIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,YFACT
20 FORMAT (3F10.5)
30 FORMAT (F10.5,I5)
READ 30,DELE,NPTS
DO 208 K=1,LREN
READ 20, HT(K),POS(K),GAM(K)
POS(K) = POS(K) + DELE
208 CONTINUE
BKG=100.
VELINC = (XHIGH - XLOW) / FLOAT(NPTS - 1)
VEL(1) = XLOW
DO 500 I = 2, NPTS
VEL(I) = VEL(I-1) + VELINC
DO 600 I = 1, NPTS
SPEC(I) = 3KG
DO 600 J = 1, LREN
IF (HT(J).EQ.0.) GO TO 609
OMEGA = VEL(I) - POS(J)
SPFC(/) = SPEC(I) - HT(J) + GAM(J) / (OMEGA*OMEGA + GAM(J)*GAM(J))
600 CONTINUE
CALL MINMAX (SPEC, SPECMIN, SPECMAX, NPTS)
YFACT = SCAL / (SPECMAX - SPECMIN)
CALL SCALE (YFACT, YFACT, XOFF, YOFF, BIASF, YSIZ, XLOW, SPECMIN)
CALL PLOT (VEL(1), SPEC(1), 0, 0)
DO 700 I = 1, NPTS
CALL PLOT (VEL(I), SPEC(I), 1, 0)
700 CONTINUE
RETURN
END
SUBROUTINE PLOTTH(SCAL,FMT,NTH)

C THIS SUBROUTINE PLOTS ADD MIXTURES OF THEORETICAL SPECTRA.
C THE SPECTRA ARE OF TWO TYPES:
C 1) A SET OF Y DATA
C 2) A SET OF LORENTZIANS
C
ACTION OF PROGRAM
1. READ IN SCALING CARD FOR Y DATA TYPE. THIS SHOULD BE
   CREATED BY PROGRAM THAT GENERATED Y DATA.
2. READ IN Y DATA TYPE SPECTRA
3. DETERMINE IF LORENTZIAN ADD MIXTURES
   ARE TO BE MIXED IN (NTH GREATER THAN 1).
4. READ IN INFORMATION CONCERNING LORENTZIANS.
5. DETERMINE AREAS UNDER ALL CURVES AND USE WEIGHTING
   FACTORS TO WEIGHT THEM.
6. ADD THE SPECTRA TOGETHER AND PLOT.
C
THE PROGRAM READS IN ONLY ONE SET OF Y DATA, AND NTH = 1
SETS OF LORENTZIAN SPECTRA. EACH LORENTZIAN SPECTRA MAY
BE COMPOSED OF UP TO TEN PEAKS.

INPUT PARAMETERS

CARD 1: (4F10.5,5)
COLUMN
1 - 19 YMIN     LOW VALUE OF Y AXIS
11 - 20 YMAX    HIGH VALUE OF Y TYPE DATA
21 - 30 XL      LOW VALUE OF X AXIS OF Y TYPE DATA
31 - 40 XH      HIGH VALUE OF X AXIS OF Y TYPE DATA
41 - 45 NPTS    NUMBER OF Y DATA POINTS

CARD 2: (FMT)  Y TYPE DATA FOR THEORETICAL SPECTRA

CARD 3: (I10,F10.5)
COLUMN
1 - 19 LREN     NUMBER OF LORENTZIANS IN THIS SPECTRA
11 - 20 FACT    WEIGHTING FACTOR FOR THIS SPECTRA
               (DECIMAL FRACTION)

CARD 4: (3F10.5) REPEAT LREN TIMES
COLUMN
1 - 19 HT       HEIGHT OF PEAK DOWN FROM BACKGROUND
11 - 20 GAM     FULL WIDTH AT HALF MAX IN CM/SEC
21 - 30 POS     POSITION OF LINE IN CM/SEC

NOTE: CARD TYPES 3 AND 4 ARE REPEATED AS A SET NTH-1 TIMES

THE WEIGHTING FACTOR FOR THE Y TYPE DATA IS
FACT(Y TYPE) = 1. - SUM OF FACT(LREN TYPE)

THE PERCENTAGE AREA UNDER THE FINAL CURVE DUE TO ANY SINGLE
CONTRIBUTION IS FACT * 100. OF THE TOTAL AREA.

COMMON/ONE/XLOW,XHIGH,3IASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
DIMENSION Y(5,512),X(512),YC(512),POS(10),GAM(10),HT(10),FACT(10)
DIMENSION FMT(10)
10 FORMAT (110,E10.5)
80 FORMAT (F10.5,25X)
READ 80, YMIN,YMAX,XL,XH,NPTS
READ FMT,(Y(1,I),I=1,NPTS)
XINC=(XH-XL)/(NPTS-1.)
C
C MAKE SURE XL IS WITHIN PLOTTING REGION. IF NOT CHOP OFF LEADING POINTS.
C
XP=XL
DO 330 I=1,NPTS
NL=I
IF(XP.GE.XLOW) GO TO 340
330 XP=XP+XINC
340 XL=XP
C
C CHECK TO SEE IF XH IS WITHIN PLOTTING REGION. IF NOT CHOP OFF TRAILING POINTS.
C
XP=XH
DO 350 I=1,NPTS
NH=I
IF(XP.LE.XHIGH) GO TO 360
350 XP=XP-XINC
360 NH=NPTS-NH+1
XH = XP
NL1 = NL + 1
X(NL1) = XL
PRINT 30,NTH,NL1,NH,XL,XH,XINC
30 FORMAT(2 ENTERING PLOTTH WITH NTH = 2I5./
1 PARAMETERS ARE:*
2 NL = 2:5,
3 NH = 2:5,
4 XL = 2:10.5,/
5 XH = 2:10.5,/
6 XINC=2:10.7)
C
C DETERMINE AREA UNDER CURVE FOR Y DATA TYPE SPECTRA AND ESTABLISH X AXIS
C
SUMT = YMAX - Y(1,NL)
DO 100 I = NL1,NH
X(I) = X(I-1) + XINC
100 SUM = SUMT +YMAX - Y(1,I)
SUMT = SUM
FACT(I) = 1.
C
C IF NTH GREATER THAN 1, READ IN LORENTZIAN INFO
C
IF(NTH.LE.1) GO TO 400
DO 390 JJ = 2,NTH
READ 10,LRE4,FACT(JJ)
PRINT 40,JJ,LRE4,FACT(JJ)
40 FORMAT (2 FOR MIXING COMPONENT #I2# COMPOSED OF #I2# LORENTZIANS, WITH A WEIGHTING FACTOR OF #F10.5,/
1# LORENTZIAN PARAMETERS#T10.5# HEIGHT#T25#HALF-WIDTH#T40# POSITION#)
C
C CALCULATE FACT FOR Y DATA TYPE SPECTRA
FACT(1) = FACT(1) - FACT(JJ)

READ IN INFO FOR THE NTH SPECTRAS LREN PEAKS

DO 370 L = 1, LREN
READ 50, HT(L), GAM(L), POS(L)
PRINT 50, HT(L), GAM(L), POS(L)
GAM(L) = (GAM(L)/2.)**2
370 FORMAT (10X,E10.3,5X,E10.3,5X,E10.3)
SUMT = 0.

CALCULATE OUT LORENTZIAN SPECTRA FOR SPECTRA NUMEEF NTH

DO 380 J = NL, NH
YL = YLREN(LREN, HT, GAM, POS, X(J))
Y(JJ, J) = YL

ACCUMULATE AREA OF SPECTRA JJ

SUMT = SUMT + YL
FACT(JJ) = FACT(JJ) / SUMT
CONTINUE

CONTINUE
FACT(I) = FACT(1) / SUM
DO 500 I = NL, NH
Y(I, I) = Y(I, I) - YMAX

ADD SPECTRA TOGETHER USING FACT WEIGHTING FACTORS

YC(I) = 0.
DO 500 J = 1, NTH
500 YC(I) = YC(I) + Y(J, I) * FACT(J)

RESCALE ADD MIXTURE AND PLOT

CALL MINMAX(YC(NL), YMIN, YMAX, NM = NL + I)
YFACT = SCAL(YMAX - YMIN)
CALL SCALE (XFAC, YFACT, XOFF, YOFF + BIASF * YSZ, XLOW, YMIN)
CALL PLOT(X(NL), YC(NL), 0, 0)
DO 320 I = NL, NH
320 CALL PLOT (X(I), YC(I), 1, 0)
RETURN
END
SUBROUTINE P2(H,SCAL,IFLAG,M,L)
C
GENERAL NQR PROGRAM TO COMPUTE 1/2-3/2 SPECTRA
C
OPTIONS EXIST FOR COMPARISON OF THEORY AND EXPERIMENT
C
OPTIONS EXIST FOR ADMIXTURES OF M1 AND E2 RADIATION

DEFINITIONS OF INPUT PARAMETERS
C
C
HAFWIT=HALF WIDTH AT HALF MAXIMUM OF ABSORPTION LINE, CM/SEC
XMO=GROUND STATE MAGNETIC G-VALUE
GR=RATIO OF EXCITED TO GROUND STATE G-VALUES G1/G0
EG=ENERGY OF NUCLEAR GAMMA RAY TRANSITION
DM1=SQUARE OF M1 MIXING COMPONENT
DE2=SQUARE OF E2 MIXING COMPONENT
DSO=SQUARE OF E2/M1 MIXING RATIO

D1,D2,D3,D4=EXPERIMENTALLY DET.0. ENERGY LEVELS FOR I=3/2 STATE,
D1 IS THE LARGEST EIGENVALUE AND THEY ARE ASSUMED TO HAVE
CENTROID AT ZERO VELOCITY
H,P10,ETA0,AO,50.0E10=INITIAL HYPERFINE PARAMETERS
H= HYPERFINE FIELD IN KOE
DELE=ISOMER SHIFT IN CM/SEC
P13=QUADROPOLE SPLITTING (INCLUDING ASYMMETRY PARAMETER) CM/SEC
ETA0=ASYMMETRY PARAMETER
AO=AZIMUTHAL ANGLE OF H W.R.T. EFG PRINC. AXIS SYSTEM
BO=POLAR ANGLE ETC

NO3=NUMBER OF COMPARISONS OF THEORY AND EXPERIMENT TO BE MADE
AT,9=ORIENTATION OF UNPOLARIZED GAMMA RAY BEAM W.R.T. EFG
PRINCIPAL AXIS SYSTEM.
M03=0 FOR POLYCRYSTALLINE SPECTRUM; POSITIVE VALUE FOR SINGLE XTAL
DP1,DETA0,DA,0B=INCREMENTAL CHANGES IN QUAD SPLITTING, ASYMMETRY
PARAM, SPH POLAR COORDS, RESP.
KCP=CONTROL INTEGER FOR INTEGRATION OPTION
0 GIVES INTEGRATION OPTION
1 GIVES COMPARISON OPTION
NA= NUMBER OF PHI ANGLES IN FIRST QUADRANT OVER WHICH INTEGRATION IS PERFORMED (EQUAL INCREMENTS)
N3= SAME AS NA EXCEPT REFERS TO THETA
NB=SAME AS NA EXCEPT REFERS TO THETA
NX=NUMBER OF PLOT POINTS
NUCLEAR MAGNETON=(94.907E-3)KEV-CM/(KOE/SEC)

******************************************************************************
C
C
***INPUT CARDS***
C
C
CARD 1 (20X,F10.5,I5)
COLUMN
21 = 30 HAFWIT
31 = 35 NX
C
CARD 2 (5F10.4)
COLUMN
1 = 10 XMO
11 = 20 GR
21 = 30 EG
31 = 40 DM1
41 = 50 DE2
C
CARD 3 (4F10.4)
COLUMN
IMPORTANT

ALL SEVEN CARDS MUST BE FURNISHED ONLY THE FIRST TIME THIS OPTION IS USED. EACH SUBSEQUENT USE OF THIS OPTION USES ONLY THE LAST THREE CARDS (CARDS 5-7) AND DOES NOT READ CARDS 1-4. THIS HOLDS TRUE FOR EACH TIME THE PROGRAM IS RUN. THE FIRST FOUR CARDS NEED ONLY BE ENTERED ONCE PER RUN.

COMMON/XL,XRR,XIASF,FSIZE,YSIZE,XCHARZ,OFF,YOFF,FACT
DIMENSION SMI(10),SMI(36)
DIMENSION P1(2,4),E(4),PI1(2,4),EA(4),PI2(2,4),DATA(20)
DIMENSION X(401),SP(401),EV(8,8)
DIMENSION EA(21),DA(21),EA2(21),DA2(21),EA3(21),EA4(21),S1(21),S2(21),S3(21),S4(21)
DIMENSION EA1(21),DQ(21),D4(21),A0(64),R0(64),A4(16),R4(16)
DIMENSION R(4,4),AT(4,4),EV(8,8),EVC(8,9)
EXTERNAL FL,F1R,F12,FOR,FMI1,FMI2,FMI3,FMI4,FMI5,FMI6,FMI7,FMI8,FMI9,FMI10
IFLAG = 1
READ 150,4AFMIT,NX
OS3 FORTRAN VERSION 3.13 02 01/11/78 0053

150 FORMAT(20X,F10.5,I5)
READ 151,XM0,GR,EG,DM1,D2

151 FORMAT(5F10.4)
PRINT 170,XM0,GR,EG,DM1,D2

170 FORMAT (6H XM0=,F10.4/5H GE=,F10.4/6H DM1=,F10.4/
*6H DE2=,F10.4)
READ 130,01,02,03,04

13 FORMAT (4F10.4)
XM=(XRR-XL)/FLOAT(NX-1)
DO 93 I=1,NX

93 X(I)=XL+FLOAT(I/-1)*XM

1015 FORMAT(3I5)
READ 101,0,1,0,2,03,04

158 FORMAT(1H0.3)401=,F10.4/5m 0,102=.F10.4/1H 93)403=,F10.4/1H ,3)404=.F
110.4)

L=0
2 CONTINUE
PRINT 3,L,M

3 FORMAT(21 CALCULATED SPECTRA FOR PLOT4,I3,5X,COLUMN*,I3,///)
READ15,4,10,ETAO,A0,99,DELE

15 FORMAT (6F10.4)
DATA(1)=M
DATA(2)=P10
DATA(3)=ETAO
DATA(4)=A0
DATA(5)=90
SAV=100.
READ 113,N03,AT,9T,MO8

113 FORMAT(IS,F15.4,F10.4,15)
DATA(6)=N08
DATA(7)=AT
DATA(8)=9T
DATA(9)=MO3
MO3=FLOAT(N03)
READ 17,0P1,DETA,DA,08

17 FORMAT (4F10.4)
DATA(10)=DP1
DATA(11)=DETA
DATA(12)=DA
DATA(13)=D3
YMIN=0.
YMAX=.04
IF(KCP) 1010,1010,1011

1011 CONTINUE
C BEGIN COMPARISON LOOP
DO 260 I6=1,NO8
S11(I6)=01
O22(I6)=02
Q33(I6)=03

260 D44(I6)=04
DO 7 K8=1,NO8
P1=P10+FLOAT(K8-1)*DP1
ETA=ETAO+FLOAT(K8-1)*DETA
A=A0+FLOAT(K8-1)*A0
B=B0+FLOAT(K8-1)*B0
CALL HEX(M1,P1,ETA,A0,SM,SM,SM0,GR,EG,WM,WE)
CALL HGR(TH,03,XM0,EG,SMG)
NSG=4
NSE=8
NCON=0
CALL CI8(SM,SM1)
CALL EIGEN(SMI,EVEC,NSE,NCON)
CALL IC8(SMI,SM1)
CALL CI4(SMG,SMG)
CALL EIGEN(SMG,GVG,NSG,NCON)
CALL IC4(SMG,SMG)
PRINT 220, (SMI,I), I=1,8
220 FORMAT(1H094P12.5)
PRINT 230, (SMG(I),I), I=1,4
230 FORMAT(1H094P12.5)
DO10 I=1,8
10 EVAL(I)=SMI(I)
EVAL(I)=SMG(I)
CHI=(EVAL(I)**2 + (EVAL(K)**2)**2*(EVAL(K)**2)**2)**2*(EVAL(K)**2)**2)
1=2
CHI=SCONV (CHI)
IF (CHI.GT.1.) GO TO 326
GO TO 325
326 IF (CHI.LT.SAV) GO TO 27
GOTO 28
27 SAV=CHI
325 CONTINUE
DO 310 I=1,8
DO 310 J=1,8
310 EV(I,J)=EVEC(I,J)
DO 320 I=1,4
DO 320 J=1,4
320 EVG(I,J)=GVG(I,J)
E01=SMG(2,2)
E02=SMG(4,4)
DO 311 I=1,4
311 E4(I)=SMG(2*I,2*I)
HZ=H
PIZ=P
ETAZ=ETA
AZ=A
EZ=E
ATZ=AT
BTZ=BT
WHZ=WH
WEZ=WE
28 CONTINUE
7 CONTINUE
DO20 I=1,4
P(I,I)=E4(I)=E01
20 P(I,I)=E4(I)=E02
DATA(14)=HZ
DATA(15)=EZ
DATA(16)=PIZ
DATA(17)=ETAZ
DATA(18)=AZ
DATA(19)=AT
DATA(20)=CHI
IF (D+1) 160, 160, 161
161 CONTINUE
CALL SM1(AT,BT,EV,EGV,P1,M03,OM1,FT1,FI1,FD0,FM1R,FM1I)
CONTINUE
IF (DE2) 162, 162, 163
CONTINUE
CALL SE2(AT, BT, ET, EV, EVG, PI2, MO3, DE2, FR21, FI2I, FR11, FI11, FR01, FI01, FM11, FM21)
CONTINUE
C
FROM SPECTRUM
DO 95 I = 1, NX
DO 95 SPEC(I) = 0.
DO 35 I = 1, NX
DO 35 K = 1, 4
SPEC(I) = SPEC(I) + FL(X(I), P(J, K) + DELE, PI(J, K) + HAFWIT)
GO TO 1020
CONTINUE
C
INTEGRATION LOOP
DO 1023 I = 1, NY
1023 SPEC(I) = 0.
NAH1 = NAH + 1
N9M1 = N9M + 1
XNAH = FLOAT(NAH)
XN9M = FLOAT(N9M)
DAR = 1.57092 / XNAH
D9R = 1.57092 / XN9M
MO9 = 1
P1 = P10
ETA = ETA0
DO 1000 I = 1, NAH1
DO 1000 J = 1, N9M1
A = (FLOAT(I - 1) / FLOAT(NAH1)) * 180.
B = (FLOAT(J - 1) / FLOAT(N9M1)) * 180.
C = 3.572958
D = 3.572958
CALL HEXTH(P1, ETA, A, 9, SM, XMO, GR, EG, WH, WE)
CALL MGR(M, A, B, XMO, EG, SM)
CALL CI8(SM, SM)
CALL EIGEN(SM, EVEC, NSE, NCON)
CALL IC8(SM, SM)
CALL EIGEN(SMG, EVG, NSG, NCON)
CALL IC4(SMG, SMG)
DO 21 I = 1, 2
DO 21 J = 1, 4
II = 2 * I
JJ = 2 * J
21 PI(I, J) = SM(JJ, JJ) - SMG(II, II)
IF (DM1) 164, 164, 165
CONTINUE
CALL SM1(AT, BT, ET, EV, EVG, PI, MO3, DM1, F1R, F1I, F0R, F01R, F1I1)
CONTINUE
IF (DE2) 166, 166, 167
CONTINUE
CALL SE2(AT, BT, ET, EV, EVG, PI2, MO3, DE2, FR21, FI2I, FR11, FI11, FR01, FI01, FM11, FM21)
CONTINUE
DO 39 I = 1, NX
DO 39 J = 1, 2
DO 39 K = 1, 4
CAL1 = FL(X(I), P(J,K) + 0ELE, PI(J,K) + HAFWIT)
CAL2 = DAR*SOB*0BR
CAL3 = FL(X(I), P(J,K) + 0ELE, PI2(J,K) + HAFWIT)

SPEC(I) = SPEC(I) + CAL2*(CAL1 + CAL3)
H7 = H
ETAZ = ETA
AZ = A
BT = B
AT = A
BTZ = B

CONTINUE

IF(W) 77, 78, 78

77 UPL/M = SPEC(I)

78 CONTINUE

DO 79 I = 1, NX

79 SPEC(I) = SPEC(I)

PRINT 399

FORMAT (# THIS IS SPEC)

PRINT 440, (SPEC(I), IH = 1, NX)

CALL MINMAX(SPEC, SPECMIN, SPECMAX, NX)

DELY = SPECMAX - SPECMIN
YFACT = SCAL/DELY
CALL SCALE (XFACT, YFACT, XOFF, YOFF+BIASF, YSIZ, XL, SPECMIN)
CALL PLOT(X(1), SPEC(1), 0, 0)
DO 2100 I = 1, NX

2100 CALL PLOT(X(I), SPEC(I), 1, 0)

PRINT 104, DELE

PRINT 102, (DATA(I), I = 1, 13)

102 FORMAT(1H0, 3H =, F10.4/1H, 4HP10 =, F10.4/1H, 5METAO =, F10.4/1M, 3HAO
1 =, F10.4/1H, 3HAO =, F10.4/2H0, 5H NO3 =, F10.4, 5H AT =, F10.4, 5H BT =, F
210.4, 5H MO3 =, F10.4/1H, 4HDP1 =, F10.4/1H, 5HDETA =, F10.4/1H, 3HDA =, F
310.4/1H, 3HDB =, F10.4)

PRINT 103, (DATA(I), I = 14, 20)

103 FORMAT(1H0, 3WHE =, F10.4/1H, 3WHE =, F10.4/1H, 3WHE =, F10.4/1H, 4METAE =,
1F10.4/1H, 2MA =, F10.4/1H, 2MA =, F10.4/6H CHI =, F10.4)

RETURN

END
SUBROUTINE SM1(ATOT, EV, EVG, PI, MOB, ODM, F1R, F1I, FOR, FM1R, FM1I)

C THIS PROGRAM COMPUTES PROBABILITIES FOR 1/2-3/2 TRANSITIONS

C ..... M TYPE
DIMENSION PI(2,4), EV(6,5), EVG(4,4)
TYPE COMPLEX(4) ALP(1,4), ALG(2,2), HFM(2,4), HFM1(2,4)
TYPE COMPLEX(4) CG111, CG120, CG13M1, CG24M1, CG230, CG221
TYPE COMPLEX(4) O11, O12, O13, O14, O15, O16
TYPE COMPLEX(4) TR1(2,4), TRM1(2,4), CON, CONJ
TYPE COMPLEX(4) CO(2,4), C1(2,4), CM1(2,4)
REAL NORM
PRINT 501
501 FORMAT(# THIS IS EVG#)
PRINT 502, ((EVG(I,J), I=1,4), J=1,4)
PRINT 503 FORMAT(# THIS IS EV#)
PRINT 504, ((EV(I,J), I=1,8), J=1,9)
504 FORMAT(1H THIS IS EV#)
AT=AT/57.2958
RT=RT/57.2958
XR=-1.
XI=0.
CG111= COMP(XR, XI)
XR=1./SORT(6.)
XI=0.
CG120= COMP(XR, XI)
XR=1./SORT(12.)
XI=0.
CG13M1= COMP(XR, XI)
CG24M1=CG111
CG230=CG120
CG221=CG13M1

SET UP EIGENFUNCTION MATRIX FOR I=1/2 STATE, ALG
ALG(1,1)= COMP(EVG(1,2), EVG(3,2))
ALG(2,2)= COMP(EVG(2,4), EVG(4,4))
ALG(1,2)= COMP(EVG(1,4), EVG(3,4))
ALG(2,1)= COMP(EVG(2,2), EVG(4,2))

SAME FOR I=3/2 STATE, ALP
901 FORMAT(1H THIS IS EV#)
ALP(JW, Iwang=1,4
901 FORMAT(1H THIS IS EV#)
ALP(JW, Iwang=1,4
COMPUTE D-MATRIX, k=1
XI=FOR(3T)
XR=FMR(3T)
D11= COMP(XR, XI)
XR=FOR(3T)
YI=0.
D11= COMP(XR, XI)
XR=FMR(3T)
XI=FMI(3T)
DM11= COMP(XR, XI)
XR=-FMR(3T)
XI=FMI(3T)
DM11= COMP(XR, XI)
XR=FOR(9T)
YI=0.
DO91=COMP(XR,XI)
XR=FIR(AT,BT)
XI=FIR(ALT,BT)
D*M1=COMP(XF,XI)
R=FOR(9T)
XI=0.
DOm1=COMP(XR,XI)
XR=FIR(AT,BT)
XI=FIR(ALT,BT)
Dm/M1=COMP(XR,XI)

SET-UP TRANSITION MATRIX CONNECTING ALP AND ALG

C
DO700I=1,2
DO700J=1,4
HR1(I,J)=COMP(0,0.)
MRM1(I,J)=COMP(0,0.)
NIR/(1.1)=CG/11011
MR1(1,2)=CG1203001
MR1(1,3)=CG13M1*DOM1
MR1(2,2)=CG221*CI1
MR1(2,3)=CG230*DI1
MR1(2,4)=CG24M1*DM1
IRM1(1,1)=OG111*01M1
HRM1(1,2)=CG120*DOM1
MR41(1,3)=CG13M1*DM1M1
MR41(2,2)=CG220*DI1
MR41(2,3)=CG230*DM1
MR41(2,4)=CG24M1*DM1

C USE MATRIX MULTIPLICATION TO OBTAIN TRANSITION MATRIX ELEMENTS
DO702I=1,2
DO702J=1,4
TR1(I,J)=COMP(0,0.)
IF (Z03.GT.0.1 GO TO 720
GO TO 719
GO TO 711

C POLYCRYSTALLINE SPECTRUM
DO 709 I=1,2
DO 709 J=1,4
CI(I,J)=CG120*CONJ(ALG(I,I))*ALP(2,J)
1 + CG230*CONJ(ALG(2,II))*ALP(3,J)
C1(I,J)=CG111*CONJ(ALG(I,II))*ALP(1,J)
1 + CG221*CONJ(ALG(2,II))*ALP(2,J)
CM1(I,J)=CG24M1*CONJ(ALG(2,II))*ALP(4,J)
1 + CG13M1*CONJ(ALG(1,II))*ALP(3,J)
X1=NORM(C0(I,J))**2
X2=NORM(C1(I,J))**2
X3=NORM(CM1(I,J))**2
709 PI(I,J)=DOM1*(X1+X2+X3)
AT=AT57.2958
BT=BT57.2958
711 CONTINUE
132 FORTRAN VERSION 3.13 01/11/79 0053

PRINT 401
401 FORMAT(2 THIS IS PI*)
PRINT 440,((PI(I/JJJ),JJ=1,4),II=1,2)
440 FORMAT(1H 0.F12.4)
RETURN
END

SUBROUTINE HGR(H,A,SMO,EG,SMG)
DIMENSION SMG(4,4)
C
CONVENTION IS THAT -1/2 CORRESPONDS TO 1, ETC
GO=(94.987E-3)*SMO/EG
GO=0.972
DO 811 I=1,4
DO 811 J=1,4
811 SMG(I,J)=0.
A=0.572958
B=3/57.2958
SMG(1,1)=-.5*COS(B)*GO
SMG(2,2)=SMG(1,1)
SMG(3,3)=SMG(1,1)
SMG(4,4)=SMG(2,2)
SMG(1,2)=-.5*SIN(B)*COS(A)*GO
SMG(2,1)=SMG(1,2)
SMG(3,4)=SMG(1,2)
SMG(4,3)=SMG(3,4)
SMG(1,4)=-.5*SIN(B)*SIN(A)*GO
SMG(4,1)=SMG(1,4)
SMG(2,3)=-SMG(1,4)
SMG(3,2)=SMG(2,3)
A=A+57.2958
B=B+57.2958
RETURN
END

SUBROUTINE CI8(SM,SMI)
DIMENSION SM(5,8),SMI(36)
C
1 M=1.3
IJ=(M*(M+1))/2
MS=M
DO 1 J=MS,5
SMI(IJ)=SM(J,M)
1 IJ=IJ+J
RETURN
END
SUBROUTINE HEX(H,P1,ETA, A, 9, SM, XM0, GR, EG, WH, WE)

DIMENSION R(4,4), AI(4,4), SM(8,8)

C NUMERICAL CONVENTION IS THAT -3/2 CORRESPONDS TO 1, ETC.

X12=1.+(ETA**2)/3.

WE=.5*P1/SQRT(X12))

WH=(9.4367E-3)*XM0*GR/EG

A=4/57.2958

B=3/57.2958

DO 1 I=1,4

DOJ=1,4

1 R(1,1)=0.

R(1,1)=-1.5*WH*COS(6)-WE

R(2,2)=-.63*WH*COS(3)-WE

R(3,3)=.5*WH*COS(8)-WE

R(4,4)=1.5*WH*COS(1)-WE

R(1,2)=(SQRT(3.)/2.)*WH*SIN(9)*COS(Al)

R(2,1)=-R(1,2)

R(2,3)=WH*SIN(6)*COS(Al)

R(3,2)=R(2,3)

R(3,4)=-R(1,2)

R(4,3)=R(3,4)

R(1,3)=(1./SQRT(3.))*ETA*WE

R(7,1)=R(1,3)

R(2,4)=R(1,3)

R(4,2)=R(1,3)

DOII=1,4

DOJ=1,4

2 AI(I,J)=0.

AI(1,2)=(SQRT(3.)/2.)*WH*SIN(9)*COS(Al)

AI(2,1)=AI(1,2)

AI(2,3)=WH*SIN(6)*COS(Al)

AI(3,2)=AI(2,3)

AI(3,4)=-AI(1,2)

AI(4,3)=AI(3,4)

DOII=I,8

DOSJ=1,8

5 SM(I,J)=0.

DOII=I,4

DOSJ=1,4

SM(I,J)=R(I,J)

K=I+4

L=J+4

5 SM(K,L)=R(I,J)

DOII=I,4

DOSJ=1,4

K=J+4

SM(I,K)=-AI(I,J)

L=I+4

6 SM(L,J)=AI(I,J)

A=A*57.2958

B=B*57.2958

RETURN
END
SUBROUTINE SE2(A, B, E2, EV, EVG, P1, MOB, DE2, FR2, FI2, FR1, FI1, F0)
C THIS PROGRAM COMPUTES PROBABILITIES FOR 1/2-3/2 TRANSITIONS ... E2
C TYPE
DIMENSION P1(2, 4), EV(3, 5), EVG(4, 4)
TYPE COMPLEX(4) CM2(2, 4), CM1(2, 4), C0(2, 4), C1(2, 4), C2(2, 4)
TYPE COMPLEX(4) TF1(2, 4), TRM1(2, 4), COMP, CONJ
TYPE COMPLEX(4) ALP(4, 4), ALG(2, 2), HR1(2, 4), HRM1(2, 4)
TYPE COMPLEX(4) CH11, CH12, CH13, CH21, CH22, CH23, CH24, CH1M1, CH1M2
TYPE COMPLEX(4) DM1, DM1M1, DM1, DM1, DM1
REAL NORM
A=A/57.2955
B=B/57.2955
XR=1./(2.*SORT(5.))
XI=0.
CH11 = COMP(XR, XI)
XR=1./SORT(10.)
CH12 = COMP(XR, XI)
XR=SORT(3.)/(2.*SORT(5.))
CH13 = COMP(XR, XI)
XR=1./SORT(5.)
CH14 = COMP(XR, XI)
CH24 = CH11
CH23 = CH12
CH22 = CH13
CH21 = CH14

C COMPUTE O-MATRIX
C XR=FRM21(A, B)
XI=FIM21(A, B)
DM21 = COMP(XR, XI)
XR=FRM11(A, B)
XI=FIM11(A, B)
DM11 = COMP(XR, XI)
XR=FR01(A, B)
XI=FIM01(A, B)
DM01 = COMP(XR, XI)
XR=FR11(A, B)
XI=FIM11(A, B)
DM11 = COMP(XR, XI)
XR=FR21(A, B)
XI=FIM21(A, B)
DM21 = COMP(XR, XI)
XR=FRM1(A, B)
XI=FIM1(A, B)
DM11 = COMP(XR, XI)
XR=FR11(A, B)
XI=FIM11(A, B)
DM11 = COMP(XR, XI)
XR=FRM1(A, B)
XI=FIM1(A, B)
DM11 = COMP(XR, XI)
XR=FR11(A, B)
XI=FIM11(A, B)
DM11 = COMP(XR, XI)
XR=FRM1(A, B)
XI=FIM1(A, B)
DM11 = COMP(XR, XI)
XR=FR11(A, B)
XI=FIM11(A, B)
DM11 = COMP(XR, XI)
XR=FRM1(A, B)
XI=FIM1(A, B)
DM11 = COMP(XR, XI)
XR=FR11(A, B)
XI=FIM11(A, B)
DM11 = COMP(XR, XI)
XR=FRM1(A, B)
XI=FIM1(A, B)
SET UP EIGENFUNCTION MATRIX FOR I=1/2 STATE, ALG

ALG(1,1) = COMP(EVG(1,2), EVG(3,2))
ALG(2,2) = COMP(EVG(2,4), EVG(4,4))
ALG(1,2) = COMP(EVG(1,4), EVG(3,4))
ALG(2,1) = COMP(EVG(2,2), EVG(4,2))

SAME FOR I=3/2 STATE, ALP

ALP(I,J,IM) = COMP(EV(I,2*IM), EV(I+1,2*IM))

DEFINE TRANSITION MATRICES

TR1(I,J) = 0.03
TR2(I,J) = 0.0

TR1(I,J) = TR1(I,J) + CONJ(ALG(I,J))*HRM1(I,J)*ALP(K,J)

TR1(I,J) = TR1(I,J) + CONJ(ALG(I,J))*HRM1(I,J)*ALP(K,J)

TR1(I,J) = TR1(I,J) + CONJ(ALG(I,J))*HRM1(I,J)*ALP(K,J)

TR1(I,J) = TR1(I,J) + CONJ(ALG(I,J))*HRM1(I,J)*ALP(K,J)

POLYCRYSTALLINE SPECTRUM
OS3 FORTRAN VERSION 3.13 SE2 01/11/78 0053

719 DO709I=1,2
    DO709J=1,4
    CM2(I,J)=CH14M2*CONJ(ALG(1,I))*ALP(4,J)
    CM1(I,J)=CH24M1*CONJ(ALG(2,I))*ALP(4,J)+CH13M1*CONJ(ALG(1,I))*ALP(1,J)
    CO1(I,J)=CH12O*CONJ(ALG(1,I))*ALP(2,J)+CH22O*CONJ(ALG(2,I))*ALP(2,1,J)
    CI1(I,J)=CH11*CONJ(ALG(1,I))*ALP(1,J)
    X1=NORM(CM1(I,J))**2
    X2=NORM(CM2(I,J))**2
    X3=NORM(CO1(I,J))**2
    X4=NORM(CI1(I,J))**2
    X5=NORM(C2(I,J))**2
CONTINUE
A=A+.57.2959
Q=Q+.57.2958
RETURN
END

FUNCTION FL(Y,W,H,G)
    FL=(H*(G**2))/(4.*((W-H)**2)+G**2)
RETURN
END

FUNCTION FIM11(A,B)
    FIM11 =-.5*(2.*COS(B)**2-COS(B)-1.)*SIN(A)
RETURN
END

FUNCTION FRM11(A,B)
    FRM11 =-.5*(2.*COS(B)**2-COS(B)-1.)*COS(A)
RETURN
END

FUNCTION FIM21(A,B)
    FIM21 =-.5*(1.-COS(B))*SIN(B)*SIN(2.*A)
RETURN
END

OS3 FORTRAN VERSION 3.13 01/11/78 0053
FUNCTION FRN21(A, 5)
  FRN21 = -.5 * (1. - COS(B)) * SIN(B) * COS(2. * A)
END

FUNCTION F1R(A, 4)
  F1R = -.5 * (1. + COS(B)) * COS(A)
END

FUNCTION FII(A, 5)
  FII = .5 * (1. + COS(B)) * SIN(A)
END

FUNCTION FOR(6)
  FOR = -SIN(B) / SQRT(2.)
END

FUNCTION FM1R(A, 5)
  FM1R = -.5 * (1. - COS(B)) * COS(A)
END

FUNCTION FM1I(A, 9)
  FM1I = .5 * (1. - COS(B)) * SIN(A) * (-1.)
END
FUNCTION FI21(A,B)
FI21 = -.5*(1.+COS(B))**SIN(B)*SIN(2.*A)
RETURN
END

FUNCTION FR21(A,B)
FR21 = +.5*(1.+COS(B))**SIN(B)*COS(2.*A)
RETURN
END

FUNCTION FI11(A,B)
FI11 = -.5*(2.*COS(B)**2+COS(B)-1.)*SIN(A)
RETURN
END

FUNCTION FR11(A,B)
FR11 = +.5*(2.*COS(B)**2+COS(B)-1.)*COS(A)
RETURN
END

FUNCTION FI01(A,B)
FI01 = 0.
RETURN
END

FUNCTION FR01(A,B)
FR01 = -SORT(3./2.)*SIN(3)*COS(3)
RETURN
END
SUBROUTINE CI4(SMG, SMGI)
DIMENSION SMG(4,4), SMGI(10)
DO 1 M=1,4
   IJ=(M*(M+1))/2
   MS=M
   DO 1 J=MS,4
      SMGI(IJ)=SMG(M,J)
1   IJ=IJ+J
RETURN
END

SUBROUTINE IC8(SMI, SM)
DIMENSION SMI(36), SM(8,8)
DO 2 I=1,8
   DO 2 J=1,8
      SM(I,J)=0.
      K=0
   DO 1 I=1,8
      K=K+1
1   SM(I,I)=SMI(K)
RETURN
END

SUBROUTINE IC4(SMG, SMGI)
DIMENSION SMGI(10), SMG(4,4)
DO 2 I=1,4
   DO 2 J=1,4
      SMG(I,J)=0.
      K=0
   DO 1 I=1,4
      K=K+1
1   SMG(I,I)=SMGI(K)
RETURN
END
140

SUBROUTINE LABELS (VAL, ARRAY, NPRINT)
VAL = ABS(VAL)
IF(VAL.GE.999.995.0R. .AND. VAL.LT. .01) GO TO 100
N = 6
ILOG = XLOG = ALOG10(VAL)
M = 4 - ILOG
IF(XLOG.LT.0.) N = 7
IF(VAL.LT.0.) N = 8
NPRINT = N - M + 2
NCHAR = N
ENCODE (6,50,FMT) N,M
50 FORMAT (F*,I1,2.t/1.)*2
JJ = IFIX((VAL +.005) * 100.)
IF(MOD(JJ,10).EQ.0) NPRINT = NPRINT -1
IF(MOD(JJ,100).EQ.0) NPRINT = NPRINT -2
GO TO 200
100 IF (VAL) 110,20,130
110 NCHAR = NPRINT = 8
FMT = 6H(E8.1)
GO TO 200
130 NCHAR = NPRINT = 7
FMT = 6H(E7.1)
200 ENCODE (NCHAR,FMT,ARRAY) VAL
RETURN
20 ARRAY = 1H0
NCHAR = NPRINT = 1
RETURN
END

SUBROUTINE YAXIS (SCAL)
COMMON/ONE/XLOW,XHIGH,BIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,FACT
COMMON/TWO/CALCON,CG,NL,XL,NH,XH,YMIN
IF(SCAL.LE.0.) GO TO 220
XP=XLOW
GO 230 J=1,2
CALL PLOT (XP,100.,0,0)
CALL PLOT (XP,100.,1.6)
IF (YMIN.LE.99.) CALL PLOT (XP,99.,1.6)
CALL PLOT (XP,YMIN,1.0)
220 SCAL = SCAL * (1.8IASF)
RETURN
C
IF NO DATA IS TO BE PLOTTED BUT THEORETICAL SPECTRA ARE,
THE Y AXIES ARE DRAWN AT THIS POINT AND THE SCALE FACTOR
IS SET = .9
C
220 SCAL = .9 * YSIZ
CALL SCALE (XFACT,1.,XOFF,YOFF,XLOW,0.)
CALL PLOT (XLOW,0.,0,0)
CALL PLOT (XLOW,0.,1.6)
CALL PLOT (XLOW,SCAL,1.0)
CALL PLOT (XHIGH,0.,0,0)
CALL PLOT (XHIGH,0.,1.6)
CALL PLOT (XHIGH,SCAL,1.0)
SCAL = SCAL * (1.-BIASF)
RETURN
END
SUBROUTINE TANDH (SCAL, T, H, XOFF)
COMMON/XLOW, XHIGH, 9IASF, XSIZE, YSIZE, CHARSZ, XOFF, YOFF, XFACT
DIMENSION FORM(3), 3CDARAY(10)
20 FORMAT(*H = t./3)
70 FORMAT(*H = t(2HT=9F4.2/I1, r)*)
CALL SCALE (XFACT, 1, XOFF, YOFF, XOFF + YOFFSET, XSIZE, XLOW, 0.)
IF (T.EQ.0.) GO TO 10
ILOG = ALOG10(T)
NFORM = 2 - ILOG
ENCODE (11, 70, FORM) NFORM
ENCODE (6, FORM, 3CDARAY) T
YTOFF = SCAL/2.
CALL SYMBOL (XTOFF, YTOFF, 0, CHARSZ, 2, 3CDARAY)
10 IF (H.EQ.0.) RETURN
YTOFF = SCAL/2. - (1.5*CHARSZ)
H = H
ENCODER (6, 20, 3CDARAY) H
CALL SYMBOL (XTOFF, YTOFF, 0, CHARSZ, 2, 3CDARAY)
XHOFF = XTOFF + CHARSZ/XFACT
CALL SYMBOL (XHOFF, YHOFF, 0, CHARSZ/2, 1, 1HE)
RETURN
END

SUBROUTINE MINMAX (ARRAY, AMIN, AMAX, N)
DIMENSION ARRAY(512)
AMIN = AMAX = ARRAY(1)
DO 10 I = 2, N
IF (ARRAY(I) .GT. AMAX) AMAX = ARRAY(I)
10 IF (ARRAY(I) .LT. AMIN) AMIN = ARRAY(I)
RETURN
END

FUNCTION YLEN(LREN, HT, GAM, POS, X)
DIMENSION HT(10), GAM(10), POS(10)
YLEN = 0.
DO 1 I = 1, LREN
XPMSQ = (X - POS(I))**2
1 YLEN = YLEN + HT(I) / (XPMSQ * GAM(I) + 1.)
RETURN
END
APPENDIX II

Program GVAL
PROGRAM GVAL(INPUT, OUTPUT)

C THIS PROGRAM INPUTS G VALUES OBTAINED FROM THE EPR SPECTRA OF AN S = 1/2 SYSTEM AND OUTPUTS THE CRYSTAL FIELD PARAMETERS D, E, AND THE ENERGY OF THE GROUND ELECTRONIC STATE. THE PROGRAM READS IN MODULUS OF THE G TENSOR AS GX, GY, AND GZ IN FREE FORM INPUT MODE AND PRINTS OUT ALL POSSIBLE REAL PERMUTATIONS OF THE G TENSOR WHICH LEAD TO REAL EIGENVECTORS. IF A GIVEN SET WILL NOT CONVERGE, WITHIN 50 ITERATIONS, A MESSAGE IS PRINTED OUT WHICH STATES THE PROBLEM. IF THE SUM GX + GY - GZ IS NEGATIVE, A REAL SET OF EIGENVECTORS CANNOT BE FOUND.

DIMENSION G(6)
REAL K
REAL *GX,GY,GZ
R2 = SORT(2.)
G(1) = GX
G(2) = -GX
G(3) = GY
G(4) = -GY
G(5) = GZ
G(6) = -GZ

20 FORMAT(1H1,\\\\\\
         '1', X, 3X, GX, X, 3X, GY, X, 3X, GZ, X, 3X, ANORM, X, 8X, A, X, 8X, B, X, 8X, C, X, 8X, K, X, 8X, D, X, 8X, E, X, 8X, ED, X, 8X, ENERGY, LAM, X, '//')
PRINT 20

C PERMUTE ALL POSSIBLE COMBINATIONS OF G VALUES
DO 90 I = 1, 6
   GX = G(I)
DO 80 J = 1, 6
   GY = G(J)
   IF(ABS(GX).EQ.ABS(GY)) GO TO 80
   DO 70 L = 1, 6
      GZ = G(L)
      IF(ABS(GX).EQ.ABS(GZ)) GO TO 70
      IF(ABS(GY).EQ.ABS(GZ)) GO TO 70

C CHECK NORMALIZATION A*A + B*B + C*C = ANORM
IF GX + GY - GZ IS NEGATIVE, ANORM WILL ALSO BE NEGATIVE AND THIS CAN ONLY HAPPEN WHEN AN IMAGINARY SET OF A, B, AND C ARE OBTAINED SINCE A, B, C ARE SUPPOSED TO BE REAL, THIS SET IS THROWN OUT

ANORM = (GX*GX + GY*GY + GZ*GZ + GX*GY + GX*GZ + GY*GZ) / (4.* (GX*GY - GX*GZ))
IF(ANORM.LT.0.) GO TO 70

SQRGT = SQRT(GZ + GY - GX)
A = (GZ + GY + GZ - GX) / (4.* SQRGT)
B = (GY - GX) / (2.* SQRGT)
C = (GX + GZ) / (4.* SQRGT)
CALL FIT1(A, B, C, K, GX, GY, GZ, IFLAG)
D = E = ENERGY = ED = 0.
IF(ED.LT.0.) CALL DEL(A, B, C, D, E, ENERGY)
   IF(D.NE.0.) ED = E/D
PRINT 40, GX, GY, GZ, ANORM, A, B, C, K, D, E, ED, ENERGY
SUBROUTINE DEL (A,B,C,D,E,EN)

C

COMPUTE CRYSTAL FIELD PARAMETERS FROM EIGENVECTOR

C

DIMENSION X(3,3),Y(3),WKAREA(16)
R2 = SORT(R2)
N=3
M = 1
IA = 3
IDGT = 6
X(1,1) = X(2,1) = X(3,1) = X(1,2) = X(2,2) = 1.
X(3,2) = -2.
X(1,3) = -3.*C/A
X(2,3) = -3.*A/C
X(3,3) = 0.
Y(1) = -.5 - B/(R2*A)
Y(2) = .5
Y(3) = A/(R2*8)
CALL LEGT1F (X,M,N,IA,Y,IDGT,WKAREA,IER)
EN = Y(1)
D = Y(2)
E = Y(3)
IF (IER.NE.0) PRINT 90,IER
FORMAT(5x,*ERROR IN SOLVING FOR D,E, AND ENERGY. ERROR CODE = I5)
RETURN
END

SUBROUTINE NORM(A,B,C)

AA = A*A
BB = B*B
CC = C*C
SUM = AA + BB + CC
SUMR = SQRT(SUM)
A = A/SUMR
B = E/SUMR
C = C/SUMR
END
SUBROUTINE FIT1 (A,B,C,K,GXEXP,GYEXP,GZEXP,IFLAG)
DIMENSION APARA(4,4), PARA(4), WKAREA(16)
REAL K
N = 4
M = 1
IA = 4
IDGT = 5
ITERC = 0
ITER = 50
IFLAG = 0
K = 1.
R2 = SQRT(2.)

C NORMALIZE INITIAL TRIAL
C
CALL NORM(A,B,C)
CONTINUE
A8 = A*A
B8 = B*B
C8 = C*C
A8C = A*C
B8C = B*C

C CALCULATE DERIVATIVES
C
DGXDA = 2.*(2.*C-R2*K*B)
DGXDB = 2.*(-2.*B + R2*K*(C-A))
DGXCC = 2.*(2.*A + R2*K * B)
DGXDK = 2.*R2*(B*C-AB)
DGYCA = 2.*(2.*C+R2*K*B)
DGYCB = 2.*(2.*B + R2*K*(C+A))
DGYDC = 2.*(2.*A+R2*K*B)
DGYDK = 2.*R2*(B*C+AB)
DGZDA = 4.*A*(1.*K)
DGZOB = -4.*B
DGZOC = 4.*C*(1.-K)
DGZDK = 2.*(AA-CC)
DONECA = 2.*A
DONECB = 2.*B
DONECOC = 2.*C
DONECDK = 0.

C CALCULATE FUNCTIONS
C
ONE = AA + B8 + CC
GX = 2.*(2.*AC - B8 + R2*K*(3C-AB))
GY = 2.*(2.*AC + B8 + R2*K*(BC+AB))
GZ = 2.*(AA - B8 + CC + K*(AA-CC))

C SET UP MATRIX FOR NEWTONS METHOD
C
APARA(1,1) = DGXDA
APARA(1,2) = DGXDB
APARA(1,3) = DGXDC
APARA(1,4) = DGXDK
APARA(2,1) = GYDA
APARA(2,2) = OGY7B
APARA(2,3) = OGYDC
APARA(2,4) = OGYDK
APARA(3,1) = OGZDA
APARA(3,2) = OGZDB
APARA(3,3) = OGZDC
APARA(3,4) = OGZDK
APARA(4,1) = DONEDA
APARA(4,2) = DONEDB
APARA(4,3) = DONEDC
APARA(4,4) = DONEDK
PARA(1) = GXEXP = GX
PARA(2) = GYEXP = GY
PARA(3) = GZEXP = GZ
PARA(4) = 1. = ONE

C ACCUMULATE SUM OF SQUARE OF RESIDUALS
C
RES = 0.
DO 200 I = 1,4
RES = RES + PARA(I)**2
200 CONTINUE
C CHECK TO SEE IF DONE OR TOO MANY ITERATIONS
C
IF(RES.LT.1.E-15) GO TO 320
IF(ITERC.GE.ITER) GO TO 310
ITERC = ITERC + 1
CALL LEOT1F(APARA,M,N,IA,PARA,IDGT,WKAREA,IER)
A = A + PARA(1)
B = B + PARA(2)
C = C + PARA(3)
K = K + PARA(4)
C IF ERROR IN SOLVING SYSTEM, TERMINATE AND SET IFLAG NEGATIVE
C
IF(IER.EQ.0) GO TO 10
PRINT 180,IER
180 FORMAT(2X*ERROR IN SOLVING FOR A,B,C, AND K. ERROR CODE = *15)
IFLAG = -1
GO TO 320
310 PRINT 300
300 FORMAT(2X*SOLVING FOR A,B,C,AND K FAILED TO CONVERGE#)
IFLAG = -1
320 RETURN
END
APPENDIX III

Program QSPLIT
PROGRAM OSPLIT(INPUT, OUTPUT)

C THIS PROGRAM CALCULATES THE ENERGY SPACING AND COEFFICIENTS OF THE
C WAVEFUNCTION FOR AN S=1/2 ELECTRONIC STATE FOR A D-5 ELECTRON
C CONFIGURATION.
C
C THE WAVE USED IS
C THAT OF J. S. GRIFFITH AND OTHERS
C
C INPUT PARAMETERS
C
D, E, XLAM = CRYSTAL FIELD AND SPIN ORBIT TERMS
XR = KAPPA USED IN CALCULATING G VALUES, AN ORBITAL
REDUCTION FACTOR.
HYPERK = KAPPA USED IN HYPERFINE CALCULATION. ORIGIN SIMILAR
TO XR.

P = MULTIPLICATIVE FACTOR FOR HYPERFINE CALCULATION.
CALCULATED FROM G * GN * BETA(N) * BETA(E) * <R**3>
COMMONLY P*HYPERK/(GN*BETA(N)) = 20G KOE (APPROX)

XYNN, XZNN, YZNN = COVALENCY FACTORS
BARN = CONSTANT IN BARNS FOR D (10**24 CM**2)
R = CONSTANT FOR <R**3> = R*A(0)**3
COMMONLY R = 5.

C THIS PROGRAM USES TWO LIBRARIES IN RUNNING. THEY ARE OBTAINED
C LOAD AS FOLLOWS
C
USER,AAS5C, -----------
CHARGE, 7251604.
ATTACH, IMSL/UN=LIBRARY.
GET, LPLTLIB/UN=AAG13C.
GET, OSULIB/UN=LIBRARY.
GET, GVALBIN.
LOSET, LIB=IMSL/LPLTLIB/OSULIB.
GVALBIN.
7/8/9
.
INPUT DECK
.
7/8/9
.
6/7/6/9

DIMENSION EQQ(3), ETA(3)
DIMENSION H(6,6), HSO(6,6), HCF(6,6), VEC(6,6), VAL(6), WK(60)
13 FORMAT(3F10.5, 10F10.5, 5F10.5)
30 FORMAT (/,* CRISTAL FIELD MATRIX, 6(6(2X.F10.3)/))
30 FORMAT (/,* SPIN ORBIT MATRIX, 6(6(2X.F10.3)/))
50 FORMAT(114, 0 = *,10.5, 2X, 10.5,5X, * LAMBDA = *,10.5,
1 /, * KAPPA = *,10.5, 2X, HYPERK = *,10.5, 5X, 2X, E = *,10.3/)
2 * HYPERK = *,10.5, 5X, 2X, E = *,10.3/)
3 5X, 2X, BARN = *,10.5, 5X, 2X, XZNN = *,10.5, 5X, 2X, YZNN = *,10.5/)
60 FORMAT (/,6X EIGENVALUE = *,G15.6,2X EIGENVECTOR = *,F10.5)
ASSIGN DEFAULT VALUES FOR PARAMETERS LEFT AS ZERO

IF (P .EQ. D.) P = .260
IF (BARN .EQ. 0.) BARN = .10
IF (R .EQ. 0.) R = 5.
IF (XYNN .EQ. 0.) XYNN = 1.
IF (XZNN .EQ. 0.) XZNN = 1.
IF (YZNN .EQ. 0.) YZNN = 1.
IF (XKAP .EQ. 0.) XKAP = 1.
IF (HYPERK .EQ. 0.) HYPERK = XKAP

START CALCULATION

PRINT 50, D, E, XLM, XKAP, HYPERK, P, XYNN, XZNN, YZNN, BARN, R
XYN = SORT(XYNN)
XZN = SORT(XZNN)
YZN = SORT(YZNN)
CALL CF(HCF, D, E)
CALL SO(HSO, XLAM)
CALL MATADD(MCFOISOpH, N)
PRINT 20, ((HCF(I, J), J = 1, N), I = 1, N)
PRINT 30, ((HSO(I, J), J = 1, N), I = 1, N)
CALL VCVFS(H9N, H)
CALL EIGRS(H9N, IJOB, VAL, VEC, N, WK, IER)
PRINT 70, WK(1), IER
PRINT 50, (VAL(I), (VEC(I, J), J = 1, N), I = 1, N)
CALL GVAL (VAL, VEC, XKAP, E/D, HYPERK, P, XYN, XZN, YZNN, R, BARN, EQQ, ETA)
CALL QSVST (VAL, EQQ, ETA, TMN, TMX, NPTS)
CONTINUE
END
SUBROUTINE CF(HCF,O,E)
DIMENSION HCF(6,6)
DO 100 I=1,6
DO 100 J=1,6
100 HCF(I,J) = 0.
HCF(1,1) = HCF(3,3) = HCF(4,4) = HCF(6,6) = 0
HCF(2,2) = HCF(5,5) = 2.* E
HCF(1,3) = HCF(3,1) = HCF(4,6) = HCF(6,4) = 3.* E
RETURN
END

SUBROUTINE SOHSO,XLAM)
DIMENSION HS0(6,6)
DO 100 I=1,6
DO 100 J=1,6
100 HS0(I,J) = 0.
XLAM2 = XLAM/2.
XLAMR2 = XLAM/SQRT(2.)
HS0(1,1) = HS0(4,4) = -XLAM2
HS0(3,3) = HS0(6,6) = XLAM2
HS0(1,2) = HS0(2,1) = -XLAMR2
HS0(4,5) = HS0(5,4) = XLAMR2
RETURN
END

SUBROUTINE MATADD(A,B,C,N)
DIMENSION A(N,N),B(N,N),C(N,N)
DO 100 I=1,N
DO 100 J=1,N
100 C(I,J) = A(I,J) + B(I,J)
RETURN
END
SUBROUTINE GVAL(VAL,VEC,XKAP,ED,HYPERK,P,XYN,XZN,YZN,R.BARN,
1  ETA)

DIMENSION VAL(6),VEC(6,6)
DIMENSION EDQO(3),ETA(3)

FORMAT (/,$ FOR DOUBLET I2$ WITH E/O =$F10.72 ANC AN EIGENVALUE =
1 $,6)4.8,/,i A = *G14.8,5X,*,B = *G14.8,5X,*,C = *G14.8,5X,/,1# GX = G14.8,5X,*,GY = *G14.8,5X,*,GZ = *G14.8,5X,
1# AX = *G14.8,5X,*,AY = *G14.8,5X,*,AZ = *G14.8,5X,1# EECO/4 = *G14.8,5X,*,ETA = *G14.8)
R2 = SORT(2.)
R22 = F2 *2.
R32 = 3.*R2
TWO7 = 2./7.
R27 = R * TWO7
R67 = 3* R27
XYNN = XYN * XYN
XZNN = XZN * XZN
YZNN = YZN * YZN
DO 100 INDEX = 2,6,2
JJ = INDEX/2
DO 20 I = 1,3
20 IF(VEC(I,INDEX).NE.0.) GO TO 30
GO TO 40
30 A = VEC(1,INDEX)
B = VEC(2,INDEX)
C = VEC(3,INDEX)
GO TO 50
40 A = VEC(4,INDEX)
B = -VE(C(5,INDEX)
C = VEC(6,INDEX)
50 AA = A*A
BB = B*B
CC = C*C
AB = A*B
AC = A*C
BC = B*C
AC2 = A * C = 2.
C11 = BB * XYN * XYN
C22 = -(AA - AC2 + CC) * XZN *XZN/2.
C33 = (AA + AC2 + CC) * YZN *YZN/2.
C12I = -(AB - BC)* XZN * XYN/R2
C13 = -(AB + BC)* YZN * XYN/R2
C23I = (AA - CC) *XZN * YZN/2.
BK2R = XKAP * B * SQRT(2.)
GX = (BK2R*(C-A) + AC2 -BB) * 2.
GY = (BK2R*(C+A) + AC2 +BB) * 2.
GZ = (XKAP*(AA-CC) + AA - BB + CC) *2.

TO DETERMINE A VALUE FOR P, THE FOLLOWING SHOULD BE NOTED.
P = 2. * G(NUC) * BETA(NUC) * ETA *<R**3>
AND
COMMONLY P*HYPERK/(GN*BETA(N)) = 200 KOE (APPROX)
FOR THE GROUND STATE HYPERFINE TENSOR, AND AX,AY,AZ WILL BE
IN CM/SEC.
AX = P*(4.*(C12I) - HYPERK * (-C11 + C22 + C33)
* + TWO7*(-C11 + C22 - 2.*C33 - 3.*C13 + 3.*C23I))
C CALCULATE THE QUADRUPOLE ETA AND EQQ/4 TERMS FOR ALL THREE LEVELS

ETA() = R67111(AA + CC)/2.*(XZNN-YZNN) - AC*(XZNN + YZNN))
Q = R27*((AA + CC)/2.*(XZNN+YZNN) - BB*(XYNN + XYNN) +
1 AC * (YZNN - XZNN))
ETA(JJ) = ETA/JQ
EQQD(JJJ) = Q*BARN*2.0226/4.

C BEGIN FINAL PRINT OUT

PRINT 90,JJ,ED,VAL(INDEX).A.B1C,GX,GY,GZ,AX,AY.AZ,
1 EQQD(JJJ), ETA(JJ)
10C CONTINUE
RETURN
END

73/74 OPT=1 TRACE

SUBROUTINE OSVST(VAL,EQQ,ETA,TMIN,TMAX,NPTS)
DIMENSION VAL(6).EQQ(3).ETA(3),T(101).0S(101)
DT = (TMAX-TMIN)/(NPTS-1)
T(1) = TMIN
DO 10 I = 2,NPTS
10 TM = T(I-1) + DT
C C NOTE THAT 1.00 1/CM = 1.4388 K
C CONST = 1.4388
DO 30 J = 1,NPTS
Z = 0.
EQQFUN = 0.
ETAFUN = 0.
DO 20 I = 1,3
EXPFUN = -(VAL(2*I)-VAL(1))*CONST/T(J)
IF(EXPFUN.LT.-675.) EXPFUN = -675.
EXPFUN = EXP(EXPFUN)
Z = Z + EXPFUN
EQQFUN = EQQFUN + EEq(I)*EXPFUN
ETAFUN = ETAFUN + ETA(I)*EXPFUN
20 CONTINUE
ETAT = ETAFUN/Z
EQQT = EQQFUN/Z
QS(JJ) = 2.* EQQT * SQRT(1.+(ETAT*ETAT/3.))
30 CONTINUE
CALL MINMAX (OS,NPTS,CISMIN,IQMIX)
CALL LFPLOT (T,OS,NPTS,TMIN,TMAX,YMIN,YMAX)
CALL AXIS (0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0,0.0)
PRINT 40,((T(J),DS(J1),J=1,NPTS)
40 FORMAT('//9710.2TIT25,$QS*,.5X,F10.515X1F10.6))
RETURN
END
SUBROUTINE LPPLOT (X,Y,N,XLOW,XHIGH,YMIN,YMAX)
DIMENSION LABEL1(3), LABEL2(3)
DIMENSION X(100), Y(100)
DATA LABEL1/"TEMPERATURE/", LABEL2/"QUADRUPOLE SPLITTING/"
20 DELY=YMAX-YMIN
IF(DELY.EQ.0.) DELY = 2.
DELY2=DELY/2.
YMAX=YMAX+DELY2
YMIN=YMIN+DELY2
YTIC=DELY2
DELY2=DELY
DELY=DELY+DELY
XTIC=DELY/4.
MARGY = 15
CALL AXIS (6, OUTPUT, 8, 6, XTIC, DELX, DELY, XLOW, YMIN, XLOW, YMIN, YMAX, YTIC, 6, 6, MARGY, UPCX, UPCY)
XXOFF=4.*UPCX
XYOFF=YMIN-2.*UPCY
YYOFF=XLOW-10.*UPCX
YPOS=YMIN
XPOS=XLOW
C
C LABEL X AXIS
C
DO 40 I=1,5
XX=XPOS-XXOFF
CALL PLOT (XX, XYOFF, 0, 1R )
ENCODE (9, 30, LABEL) XPOS
40 FORM (E9.2)
CALL LABELP (9, 0, 0, LABEL)
40 XPOS=XPOS+XTIC
C
C LABEL Y AXIS
C
DO 50 I=1,5
CALL PLOT (XXOFF, YPOS, 0, 1R )
ENCODE (9, 30, LABEL) YPOS
CALL LABELP (9, 0, 0, LABEL)
50 YPOS=YPOS+YTIC
C
C PLOT DATA
C
DO 60 I=1,N
XX=XLOW+(DELY/2.)-(5.*UPCX)
XYOFF=XXOFF-2.*UPCY
YYOFF=XXOFF-2.*UPCX
CALL PLOT (XX, YYOFF, 0, 1R )
CALL LABELP (11, 0, 0, LABEL1)
60 YPOS=YPOS+DELX/2.*UPCY
YPOS=YYOFF-2.*UPCX
CALL PLOT (XXOFF, YPOS, 0, 1R )
CALL LABELP (20, 0, 1, LABEL2)
RETURN
END
APPENDIX IV

Program RELAX
PROGRAM RELAX (INPUT, OUTPUT, PUNCH, TAPE10)
C
THIS PROGRAM CALCULATES RELAXATION SPECTRA FOR S=1/2 ELECTRONIC
SPIN AND GENERAL HYPERFINE INTERACTION AX, AY, AZ. ORIGINAL
PROGRAM BY G. K. SHENOY AT ARGONNE NATIONAL LAB.
C
*****************************************************************************

C INPUT PARAMETERS AND ARRAYS
C
YC(I) = COMPUTED RELAXATION SPECTRUM
GX,GY,GZ= ELECTRONIC S=1/2 G VALUES
RG = NUCLEAR G FACTOR RATIO
AXG,AYG,AZG = NUCLEAR GROUND STATE A TENSOR
AXE,AYE,AZE = NUCLEAR EXCITED STATE A TENSOR
EQ = QUADRUPOLE PARAMETER(=**2*Q/16).
ETA QUADRUPOLE ASSYMETRY PARAMETER
VJ = RELAXATION RATE
ALFA,BETA,GAMMA = EULER ANGLES FOR QUARRUPOLE TENSOR

C INPUT INFORMATION

CARD 11 (210,2F10.5,110)
COLUMN
1 - 10 NSPEC......NUMBER OF DISTINCT SPECTRA PARAMETER
SETS TO RAD IN
11 - 20 I P L O T .......FLAG FOR CALCOMP PLOTS
IPLOT = 0...NO CALCOMP PLOT
IPLOT = 1...CALCOMP PLOT DONE
IPLOT = 4...PLOT DONE ON GERBER
21 - 30 XLOW.......LOW VALUE OF X AXIS IN CM/SEC
(DEFAULT = -.5)
31 - 40 XHIGH.......HIGH VALUE OF X AXIS IN CM/SEC
(DEFAULT = .5)
41 - 50 IPUNCH......IF IPUNCH IS NONZERO, A PUNCH DECK
CONTAINING AN AUTOSCALE CARD AND
Y VALUES OF THE FINAL SPECTRA IS PUNCHED

CARD 21 (15)
COLUMN
1 - 5 LREN.......NUMBER OF LORENTZIANS IN MODEL OF DATA
IF LREN = 0...OMIT CARDS 3 AND 4

CARD 31 (3E10.4)
COLUMN
1 - 10 BKG........BACKGROUND OF LORENTZIAN MODEL

(==) CARD 41 (3E10.4)
COLUMN
1 - 10 HT..........HEIGHT OF LORENTZIAN PEAK
11 - 20 GAM........FULL WIDTH AT HALF MAXIMUM (CM/SEC)
21 - 30 POS........POSITION IN CM/SEC OF PEAK

(==) CARD 51 (110)
COLUMN
1 - 10 IFLAG......FLAG FOR READING INCREMENTS
C IF IFLAG = 1 NO INCREMENTS READ
C (OMIT CARDS 10 - 13)
C IF IFLAG = 2 INCREMENTS READ AND OPTIMIZATION PERFORMED ON
C INCREMENTED PARAMETERS
C (INCLUDE CARDS 10 - 13)

C C C C
C I (== CARD 61 (4E10.4)
C C
C COLUMN
C 1 - 10 A************
C 11 - 20 B************GROUND STATE ELECTRONIC WAVEFUNCTION
C 21 - 30 C************(CM/SEC)
C 31 - 40 XKAP*******K IN G TENSOR CALC
C
C C C C
C I (== CARD 71 (5E10.4)
C C
C INITIAL COLUMN
C VALUES OF
C 1 - 10 QS**********QUADRUPOLE SPLITTING (CM/SEC)
C 11 - 20 ETA**********QUADRUPOLE ETA PARAMETER
C 21 - 30 DEL**********ISOMER SHIFT (CM/SEC)
C 31 - 40 VJ2**********RELAXATION PARAMETER (CM/SEC)
C 41 - 50 WID*******FULL WIDTH AT HALF MAXIMUM (CM/SEC)
C
C C C C
C I (== CARD 81 (5E10.4)
C C
C COLUMN
C 1 - 10 HYPERK*****KAPPA IN CALC OF A TENSOR
C 11 - 20 PK**********PKAPPA/G(NUC)*BETA(NUC) IN KCE
C 21 - 30 XYNN********
C 31 - 40 XZNN******COVALENCY FACTORS
C 41 - 50 YZNN******
C
C C C C
C I (== CARD 91 (4E10.4)
C C
C COLUMN
C 1 - 10 A************GROUNDO STATE ELECTRONIC WAVEFUNCTION
C 21 - 30 C**********(CM/SEC)
C 31 - 40 XKAP*******K IN G TENSOR CALC
C
C C C C
C I (== CARD 101 (5E10.4)
C C
C COLUMN
C 1 - 10 QS**********QUADRUPOLE SPLITTING (CM/SEC)
C 11 - 20 ETA**********QUADRUPOLE ETA PARAMETER
C 21 - 30 DEL**********ISOMER SHIFT (CM/SEC)
C 31 - 40 VJ2**********RELAXATION PARAMETER (CM/SEC)
C 41 - 50 WID*******FULL WIDTH AT HALF MAXIMUM (CM/SEC)
C
C C C C
C I (== CARD 111 (5E10.4)
C C
C COLUMN
C 1 - 10 HYPERK*****KAPPA IN CALC OF A TENSOR
C 11 - 20 PK**********PKAPPA/G(NUC)*BETA(NUC) IN KCE
C 21 - 30 XYNN********
C 31 - 40 XZNN******COVALENCY FACTORS
C 41 - 50 YZNN******
C
C C C C
C COMMON/ONE/PARA1(12)
C COMMON/TWO/X(301),XLow,XHIGH
COMMON/THREE/YC(301),YCMIN,YCMAX
COMMON/FOUR/ YL(301),YLMIN,YLMAX,AREAL
COMMON/FIVE/ YD(301),YDMIN,YDMAX
COMMON/SIX/ YCF(301),YCFMIN,YCFMAX
COMMON/SEVEN/YDF(301),YDFMIN,YDFMAX
COMMON/EIGHT/ PARA(2,14)
DIMENSION INDEX(14),BCDOUT(10)
DATA INDEX /14m0/
READ 30,NSPEC.IPLOT,XLOW,XHIGH

C CALCULATE THE X AXIS
X(1) = XLOW
XINC = (XHIGH-XLOW)/300.
DO 10 I=2,301
10 X(I) = X(I-1.) + XINC
CALL LORENTZ(LREN)
DO 600 IJ = 1,NSPEC
PRINT 40
FORMAT (1HL)
ICOUNT = 0
CHI = CHIOLD = .E15
READ 100,IFLAG,((PARA(I,J).J=1,14).I=1,IFLAG)
100 FORMAT (I10,/,((4E10.4/,5E10.4/,5E10.4))
IF(IFLAG.E0.2) GO TO 150
C SET UP PARAMETERS FOR NO VARIATION OF PARAMETERS
ICOUNT = 1
INDEX(I1) = 1
GO TO 210
150 CONTINUE
DO 200 I=1,14
IF (PARA(2,I).EQ. 0.0) GO TO 200
ICOUNT = ICOUNT + 1
INDEX(ICOUNT) = I
200 CONTINUE
C SET UP PARAMETERS FOR FIRST TIME THRU VARIATION LOOPS
I3 = INDEX(I2)
PBEST = PINT = PARA(1,I3)
DELTA = PARA(2,I3)
PRINT 20
FORMAT (1HL)
IF(I1.NE.1.OR.I2.NE.1) GO TO 270
C IF FIRST TIME THRU PARAMETER VARIATION WE NEED A CHI FOR INITIAL
C PARAMETERS SO CALCULATE SYSTEM FOR INITIAL PARAMETERS. OTHERWISE
C GO TO PARAMETER VARIATION SECTION AND THEN COME BACK HERE.
C
250 CALL PCALC
   CALL FERLX(EQ)
   IF(LREN.NE.0) CALL COMPAR(CHI)
C
IF THIS SET OF PARAMETERS WAS BETTER, STORE THE NEW SPECTRA.
C
IF NOT, CHANGE THE METHOD OF GETTING NEW PARAMETERS.
C
IF(CHI.GT.CHIOLD) GO TO 300
PBEST = PARA(1,I3)
CHIOLD = CHI
EQOLD = EQ
260 CONTINUE
   YDF(I) = YD(I)
   YCF(I) = YC(I)
   YDFMIN = YDFMIN
   YCFMAX = YCFMAX
   YDFMIN = YDFMIN
   YCFMAX = YCFMAX
   IF(2FLAG.EQ.1) GO TO 500
C
SINCE WE GET HERE AFTER THE FIRST CALC OF THE SPECTRA, VARY THE
C
I3 PARAMETER BY THE APPROPRIATE INCREMENT, AND CALCULATE AGAIN.
C
270 PARA(1,I3) = PARA(1,I3) + DELTA
   GO TO 250
C
THIS NEXT CODE CAN BE CONFUSING, BUT THE LOGIC IS REALLY SIMPLE
C
AFTER YOU THINK ABOUT IT.
C
THE PROGRAM GOES TO 300 WHEN THE LATEST GUESS IS WORSE THAN
C
THE PREVIOUS ATTEMPT, THEREFORE IT MUST BE
C
INCREMENTING IN THE WRONG DIRECTION. IF PBEST, THE VALUE
C
OF THE VARYING PARAMETER WHICH YIELOED THE BEST CHI, IS
C
NOT EQUAL TO THE VALUE BEFORE WE STARTED VARYING THE
C
PARAMETER WE HAVE GONE THRO A MINIMUM IN CHI AND PBEST IS THE
C
BEST WE CAN DO FOR THIS INCREMENT SIZE. IF, HOWEVER, THE
C
BEST VALUE IS ALSO THE INITIAL ONE, WE ARE PROBABLY
C
CHANGING THE PARAMETER IN THE WRONG DIRECTION AND NEED TO
C
GO THE OTHER WAY TO FIND THE MINIMUM IN CHI, SO DO THAT.
C
IF WE HAVE GONE BOTH WAYS (DELTA.NE.PARA(2,I3)) THEN WE ARE
C
DONE.
C
300 IF(PBEST.NE.PINT) GO TO 490
   IF(DELTA.NE.PARA(2,I3)) GO TO 490
   DELTA = -DELTA
   PARA(1,I3) = PINT + DELTA
   GO TO 250
C
WE HAVE NOW FOUND THE BEST VALUE FOR THE I3 PARAMETER WITH THE GIVEN
C
STEP SIZE AND PARAMETER SET.
C
490 CHI = CHIOLD
   PARA(112) = EQOLD
   PARA(1,13) = PBEST
   CALL PCALC
500 CALL PLOTTER(CHI,LREN)
IF (IPLT.EQ.0) GO TO 580
CALL PLOTYPE(IPLT-1)
CALL PLOTYPE(0)
YDIF = YCFMAX - YCFMIN
YMAX = YCFMAX + .5*YDIF
YMIN = YCFMIN - .5*YDIF

C PLOT SPECTRA ON PLOTTER IF REQUESTED
C
CALL PLODAT (X,YCF,301,YMIN,YMAX,X(1),X(301),0.5,6.5)
YDIF = YDIF/15.
YOFF = YMAX*YDIF
ENCODE (64,2010,BCDOUT) (PARA1(I),I=1,3)
CALL SYMBOL (X(1),YOFF,0...12,64,BCDOUT)
YOFF = YOFF - YDIF
ENCODE (64,2020,BCDOUT) (PARA1(I),I=4,6)
CALL SYMBOL (X(1),YOFF,0...12,64,BCDOUT)
YOFF = YOFF - YDIF
ENCODE (64,2030,BCDOUT) (PARA1(I),I=7,9)
CALL SYMBOL (X(1),YOFF,0...12,64,BCDOUT)
YOFF = YOFF - YDIF
ENCODE (64,2040,BCDOUT) (PARA1(I),I=10,12)
CALL SYMBOL (X(1),YOFF,0...12,64,BCDOUT)

2010 FORMAT ( /X,AYG=X,F12.7,*,AZG=*,X,F12.7)  
2020 FORMAT ( /X,GX=*,F12.7,*,GZ=*,X,F12.7)  
2030 FORMAT ( /X,GX=*,F12.7,*,ETA=*,X,F12.7,*,IS=*,X,F12.7)  
2040 FORMAT ( /X,VJ2=*,F12.7,*,MID=*,F12.7,*,MED=*,X,F12.7)  
CALL PLOTEND

580 IF(IFUNCEQ.0) GO TO 600
NPTS = 301
PUNCH 590,YCFMIN,YCFMAX,XLOW,XHIGH,NPTS,(YCF(J),J=1,301)
590 FORMAT (2F10.4,2F10.5,15,/,15F10.4)
KPUNCH = SLPUNCH
ENDFILE KPUNCH

600 CONTINUE
END
SUBROUTINE PCALC
COMMON/ONE/ PARA(1,12)
COMMON/EIGHT/ PARA(2,14)
DATA GBHN/1.18548 E-03/
HYPERK = PARA(1,10)
P = PARA(1,11) * GBHN / HYPERK
XYN = SORT(PARA(1,12))
XZN = SORT(PARA(1,13))
YZN = SORT(PARA(1,14))
IF(YZN.EQ.0.) YZN = XZN
A = PARA(1,1)
B = PARA(1,2)
C = PARA(1,3)

90 FORMAT (//: A=",F9.6",2X:2=F9.6,2X:*C=",F9.6,2X:*PistF9.6,2X:*PK=",F8.3)
R2 = SCRT(2.)
TWO7 = 2./7.
50 AA = AA
BB = B*B
CC = C*C

AC = A*C
BC = B*C

AC2 = A * C + 2.
C11 = BB + XYN * XYN
C22 = -(AA + AC + CC) * XZN * XZN/2.
C33 = (AA + AC + CC) * YZN * YZN/2.
C12 = -(AB - BC) * XZN * XYN/R2
C13 = -(AB + BC) * YZN * XYN/R2
C23 = (AA - CC) * XZN * YZN/2.

BKR2 = XKAP * B * R2
GX = (BKR2*(C-A) + AC2 - BB) + 2.
GY = (BKR2*(C+A) + AC2 + BB) + 2.
GZ = (XKAP*(AA-CC) + AA - BB + CC) *2.

TO DETERMINE A VALUE FOR P, THE FOLLOWING SHOULD BE NOTED.
IF
P = 2. * G(NUC) * BETA(NUC) * BETA * <R**-3>
AND
NOTING THAT (FROM G. LANG)
P * HYPERK/ (G(NUC)*BETA(NUC)) = 200koe (APPROX)
FOR THE GROUND STATE HYPERFINE TENSOR, AND AX, AY, AZ WILL BE
IN CM/SEC.
AX = P**4. * ( C12I - HYPERK * (-C11 + C22 + C33)
+ TWO7 * (-C11 + C22 - 2.*C33 - 3.*C11 + 3.*C23I))
AY = P**4. * (-C11 ) - HYPERK * ( C11 + C22 + C33)
+ TWO7 * ( C11 - 2.*C22 + C33 + 3.*C12I - 3.*C23I)
AZ = P**4. * ( C23I + HYPERK * ( C11 + C22 - C33)
- TWO7 * (-2.*C11 + C22 - C33 - 3.*C12I - 3.*C13 )

BEGIN FINAL PRINT OUT
PRINT 90,A,B,C,XYN,XZN,YZN,HYPERK,F,PARA(1,11)
SUBROUTINE LORENTZ(LREN)
COMMON/TWO/X(301)
COMMON/FOUR/YL(301),YLMIN,YLMAX,AREAL
DIMENSION HT(12),POS(12),GAM(12)
NP=301

C INTRODUCE THE LORENTZIAN INFORMATION IF DESIRED
C
901 READ 5,LREN
9 FORMAT(I9)
IF(LREN.EQ.0) RETURN
10 FORMAT(3E10.4)
READ 10,HT(I),GAM(I),POS(I),I=1,LREN)
PRINT 905,LREN,BKG
905 FORMAT(1X,I4,5X,F10.6,9X,F10.8)
AREAL = O.
DO 930 I = 1,NP
F = 0.
DO 920 J = 1,LREN
Z = X(I) - POS(J)
Z = Z * Z
920 F = HT(J)/((Z**GAM(J)) + 1.) + F
AREAL = AREAL + F
930 PRINT 935
935 FORMAT(* LORENTZIAN MODEL FOR DIFFERENCE CALCULATIONS: X//=)
CALL MINMAX (YL,YLMIN,YLMAX)
CALL MCSSPLT (YL,25,NP,5,10,YLMIN,YLMAX)
RETURN
END

PARA1(1) = AX
PARA1(2) = AY
PARA1(3) = AZ
PARA1(4) = GX
PARA1(5) = GY
PARA1(6) = GZ
PARA1(7) = PARA(1,5)
PARA1(8) = PARA(1,6)
PARA1(9) = PARA(1,7)
PARA1(10)= PARA(1,8)
PARA1(11) = PARA(1,9)
PARA1(12) = O.
RETURN
END
SUBROUTINE FERLX(EQQ)

COMMON/ONE/PARA1(12)
COMMON/TWO/XD(301)
COMMON/THREE/YC(301).YCMIWCMAX
COMPLEX VAL(32). VEC(32,32)
DIMENSION WORK(2500)
DIMENSION WC(32)

COMMON Q21,Q22,Q21STR,Q22STR,EXPG1,EXPG2,EXPG3,EXPG4
COMPLEX H(32,32),P,VIM(32)
EQUIVALENCE (AXG,PARA1( 1)),(AYG,PARA1(2)19(AZG,PARA1(3))
EQUIVALENCE (GX,PARA1(4)),(GY,PARA1(5)),(GZ,PARA1(6))
EQUIVALENCE (OS, PARA1(7)).(ETA,PARA1(8)).(DELE.PARA1(9))
EQUIVALENCE (VJ2,PARA1(10)).(WIO.FARA1(11)).(EQ,PARA1(12))
RG = -0.5714
AXE = AXG * RG
AYE = AY6 * RG
AZE = AZG * RG

DEFINE THE QUADRUPOLE TENSOR IN TERMS OF SPHERICAL TENSOR COMPONENTS AND EULER ANGLES SPECIFYING ORIENTATION IN MAGNETIC HYPERFINE TENSOR SYSTEM.

RADOEG = ATAN(i)/45.
BETA = 0.
GAMA = 0.
ALFA = 0.
GAMA = GAMA*RADOEG
CSB = COS(BETA)
SNB = SIN(BETA)
CSA = COS(ALFA+ALFA)
SNA = SIN(ALFA+ALFA)
Q20 = 0.5 * (3.*CSA*CSB-1.0+ETA*SNB*SNA)*CSA
GAMA2 = GAMA+GAMA

EXPG1 = CMPLX(COS(GAMA),-SIND(GAMA))
EXPG2 = CMPLX(COS(GAMA2),-SIND(GAMA2))
EXPG3 = CONJG(EXPG1)
EXPG4 = CONJG(EXPG2)
Q11 = EXPG1*CMPLX(.5*ETA*SNB*SNA,.5*SNB*CSA)
Q11STR = EXPG3 - CMPLX(-.5* ETA*SNB*SNA,.5*SNB*CSA)
Q22 = EXPG2*CMPLX(-.5*ETA*SNB*SNA,.5*SNB*SNB+25*ETA*CSA)
HZ = 0.

S = 0.
GAMA = WIO/2.
EQ = EQ / (SQRT(1.+(1.*(ETA*ETA/3.)
PRINT 141, QS,ETA,DELE
141 FORMAT (1H092 OS = 2,F12.7,* ETA= 2,F12.7,* IS = 2,F12.7)
PRINT 133,AZG,AYG,AXG
133 FORMAT (1X,* AZ = 2,F12.7,* AY = 2,F12.7,* AX = 2,F12.7)
PRINT 134, VJ2,WID,EQ
134 FORMAT (1X,* WJ2 = 2,F12.7,* WID = 2,F12.7,* EQ = 2,F12.7)
PRINT 236,GX,GY,GZ
236 FORMAT (1X,* GX = 2,F12.7,* GX = 2,F12.7,* GX = 2,F12.7)
PARAMETERS FOR ELECTRONIC SPIN MULTIPLICITIES ASSOCIATED WITH
THE NUCLEAR LEVELS

RSG = .5
RSE = .5
RSG1 = RSG + 1.
RSE1 = RSE + 1.
NSZG = 2.*RSG + 1.00001
NSZE = 2.*RSE + 1.00001

NUCLEAR SPIN MULTIPLICITY PARAMETERS

RIG = .5
RIE = 1.5
RIG1 = RIG + 1.
RIE1 = RIE + 1.
NIZG = 2.*RIG + 1.00001
NIZE = 2.*RIE + 1.00001

QUADRUPOLE PARAMETER

ROG = EQ/(4.*RIG*(2.*R/G-1.))
ROG = 0.
ROE = EQ/(4.*RIE*(2.*RIE - 1.))
NMAT = 32
DO 511 I = 1,NP

DEFINE EFFECTIVE RELAXATION RATES

WX = .5 * GX*GX*VJ2
WY = .5 * GY*GY*VJ2
WZ = .5 * GZ*GZ * VJ2
SS = .001
T = 1.
Z = 0.
K = 3
DO 2 ISG = 1,NSZG
SZG = FLOAT(ISG)-RSG1
DO 2 ISE = 1,NSZE
SZE = FLOAT(ISE)-RSE1
DO 2 IIG = 1,NIZG
ZIG = FLOAT(IIG)-RIG1
DO 2 IIE = 1,NIZE
ZIE = FLOAT(IIE) - RIE1
L = 0
K = K+1

DO 2 ISGP = 1,NSZG
SZGP = FLOAT(ISGP)-RSG1
DO 2 ISEP = 1,NSZE
SZEFP = FLOAT(ISEP) - RSE1
DIAGONAL TERMS OF H* .............

NSG = ABS(SZG - SZGP) + SS
NSE = ABS(SZE - SZE1) + SS
NIG = ABS(ZIG - ZIGP) + SS
NIE = ABS(ZIE - ZIEP) + SS

SELECTION RULE

IF (NSG .EQ. 0. AND. NSE .EQ. 0. AND. NIG .EQ. 0. AND. NIE .EQ. 0.)
  H(K,L) = CMPLX(Z,Z)

OFF DIAGONAL TERMS OF H* ...........

NSP = ABS(SZGP - SZGPL) + SS
NSM = ABS(SZG - SZGMI) + SS
NIP = ABS(ZIGP - ZIGPL) + SS
NIM = ABS(ZIG - ZIGMI) + SS

QUADRUPOLE GROUND STATE ...........

IF (NSG .NE. 0.) GO TO 1600
  XP1 = 0.
  XM1 = 0.
  IF (NIF .NE. 0.) GO TO 135
XP1 = (RIG\*RIG + ZIG\*ZIGPL)  
FCT = (ZIGPL + ZIG) \* SORT(XP1) \* ROG  
H(K,L) = H(K,L) + FCT*Q21  

135 IF(NIP.NE.0) GO TO 140  
XM1 = (RIG\*RIG + ZIG\*ZIGMI)  
FCT = (ZIGMI + ZIG) \* SORT(XM1) \* ROG  
H(K,L) = H(K,L) + FCT*Q21*STR

140 XP1 = 0.  
XM1 = 0.  
ZIGPL2 = ZIG + 2.  
ZIGMI2 = ZIG - 2.  
NIP2 = ABS(ZIGP - ZIGPL2) + SS  
NIM2 = ABS(ZIGP - ZIGMI2) + SS  
IF(NIP2 .NE.0) GO TO 145  
XP1 = (RIG - ZIG)\*(RIG + ZIG)\*(RIG - 1. - ZIG)\*(RIG + ZIGPL2)  

145 IF (NIM2 .NE.0) GO TO 150  
XM1 = (RIG + ZIG)\*(RIG1 - ZIG)\*(RIG - 1. + ZIG)\*(RIG - ZIGMI2)  

150 FCT1 = SORT(XP1) \* ROG  
FCT2 = SORT(XM1) \* ROG  
H(K,L) = H(K,L) + FCT2*Q22 + FCT1*Q22*STR

1600 CONTINUE  
C
C
C
XP1 = 0.  
XM1 = 0.  
IF(NSP.NE.0 .OR. NIG.NE.0) GO TO 2000  
SZEPL = SZE + 1.  
SZE1 = SZE + 1.  
ZIEPL = ZIE + 1.  
ZIE1 = ZIE + 1.  
NSP = ABS(SZEP - SZEPL) + SS  
NSM = ABS(SZEP - SZE1) + SS  
NIP = ABS(ZIEP - ZIEPL) + SS  
NIM = ABS(ZIEP - ZIE1) + SS  
IF(NSP.NE.0 .OR. NIP.NE.0) GO TO 180  
XP1 = (RSE*RSE - SZE*SZEPL)\*(RIE*RIE - ZIE*ZIEPL)  

180 IF(NSM.NE.0 .OR. NIP.NE.0) GO TO 190  
XM1 = (RSE*RSE - SZE*SZE1)\*(RIE*RIE - ZIE*ZIE1)  

190 FCT = -(AXE + AYE)\*(SORT(XM1) + SORT(XP1))/4.  
H(K,L) = H(K,L) + CMPLX(Z,FCT)  
XP1 = 0.  
XM1 = 0.  
IF(NSP.NE.0 .OR. NIP.NE.0) GO TO 195  
XP1 = (RSE*RSE - SZE*SZEPL)\*(RIE*RIE - ZIE*ZIEPL)

195 IF(NSM.NE.0 .OR. NIM.NE.0) GO TO 200  
XM1 = (RSE*RSE - SZE*SZE1)\*(RIE*RIE - ZIE*ZIE1)

200 FCT = -(AXE + AYE)\*(SORT(XM1) + SORT(XP1))/4.  
H(K,L) = H(K,L) + CMPLX(Z,FCT)  
C
C
C QUADRUPOLE FOR EXCITED STATE  .........  
C
C
C
IF(NSP.NE.0) GO TO 2000  
XP1 = 0.  
XM1 = 0.  
IF(NIP.NE.0) GO TO 225
XP1 = (RIE*RIE1-ZIE*ZIEPL)  
FCT = -(ZIEPL+ZIE)*SQRT(XP1)*RQE  
H(K,L) = H(K,L) + FCT*Q21
225 IF(NIM*NE.0) GO TO 240  
XM1 = (RIE*RIE1-ZIE*ZIEMI)  
FCT = -(ZIEMI+ZIE)*SQRT(XM1)*RQE  
H(K,L) = H(K,L) + FCT*Q21STR
240 XP1 = 0.  
XM1 = 0.  
ZIEPL2 = ZIE + 2.  
ZIEMI2 = ZIE - 2.  
NIP2 = ABS(ZIEP-ZIEPL2) + SS  
NIM2 = ABS(ZIEP-ZIEMI2) + SS  
IF(NIP2.NE.0) GO TO 250  
XP1 = (RIE-ZIE)*(RIE1+ZIE) P(RIE-1.-ZIE)*(RIE+ZIEPL2)  
250 IF(NIM2.NE.0) GO TO 260  
XM1 = (RIE+ZIE)*(RIE1-ZIE)*(RIE-1.+ZIE)A(RIE-ZIEMI2)  
260 FCT1 = -SQRT(XP1)*RQE  
FCT2 = -SQRT(XM1)*RQE  
H(K,L) = H(K,L) + FCT2*Q22 + FCT1*Q22STR
2800 CONTINUE
C
C TERMS OF RELAXATION MATRIX
C
IF(NIE.NE.0.OR.NIG.NE.0) GO TO 300  
IF(NSE.NE.0.OR.NSG.NE.0) GO TO 22C  
FCT = (2.*SZG*SZE-.5)-.5*(wx+wv)  
H(K,L) = MA) + CMPLX(FCT,Z)  
GO TO 300
22C CONTINUE  
FCT = 0.  
IF(S2G+SZE.LT.0.0.AND.SZGP*SZE.LT.1.0) FCT = .5*(wx+wv)  
IF(S2G+SZE.GT.0.0.AND.SZGP*SZE.GT.1.0) FCT = .5*(wx+wv)  
H(K,L) = H(K,L) + CMPLX(FCT,Z)  
300 CONTINUE
C
H(K,L) = -H(K,L)
C
2 CONTINUE
P = CMPLX(GAMMA,-S)  
DO 4 J = 1,NMAT
4 H(J,J) = H(J,J) + P
IJOB = 2  
CALL EIGCC (M,NMAT,NMAT,IJOB,VAL,VEC,NMAT,WORK,IER)  
PRINT 3012, WORK(1),IER
3012 FORMAT(# PREFORMANCE CODE = #,F13.5,5X,#ERROR CODE = #IS,/)  
DO 460 J = 1,NMAT
460 VNORM = 0.  
DO 455 I = 1,NMAT  
VECSQ = CABS(VEC(I,J))  
455 VNORM = VNORM +VECSQ*VECSQ  
VNORM = SQRT(VNORM)  
DO 458 I = 1,NMAT
VEC(I,J) = VEC(I,J)/VNORM

CONTINUE

INCLUDE INTENSITIES

DO 47 MM = 1,3
MD = MM - 2
K = 0
DO 100 ISG = 1,NSZG
SZG = FLOAT(ISG)-RSG1
DO 100 ISE = 1,NSZE
SZE = FLOAT(ISE)-RSE1
ZIG = FLOAT(IIG)-RIG1
DO 100 IIE = 1,NIZE
ZIE = FLOAT(IIE)-RIE1
L = 0
K = K+1
WC(K) = 0.
K = K+1
NS = ABS(SZG-SZE) + SS
DIF = ZIG - ZIE
IF (DIF .LT. C.) SS = -.001
NI = ZIG-ZIE + SS
IF (NI .NE. 0. OR. NI .NE. MD) GO TO 100
WC(K) = FUM(ZIG, ZIE)
CONTINUE

DO 13 K = 1,NMAT
VIM(K) = CMPLX(Z,Z)
VM(K) = VIM(K)
DO 13 L = 1,NMAT
VIM(K) = VIM(K) + WC(L) * VEC(L,K)

ADD ISOMER SHIFT (DELE) INFORMATION

P = CMPLX(Z,XD(I) - DELE)
DO 41 K = 1,NMAT
H(K,K) = VAL(K) - P
FP = FP + REAL(VM(K)*VIM(K)/H(K,K))
YC(I) = YC(I) + FP
CONTINUE
CONTINUE
CALL MINMAX(YC,YCMIN,YCMAX)
RETURN
END
FUNCTION FUN(G,E)
SS = .001
NO = ABS(E-G) + SS
IF(NO.EQ.2) FUN = 0.
IF(NO.EQ.2) RETURN
IF(NO.EQ.0) FUN = SQRT(1./6.1)
IF(NO.EQ.0) RETURN
IF(NO.EQ.1) FUN = SQRT(1./12.)
IF(NO.EQ.1.AND.E.GT.1.000.OR.E.LT.-1.000) FUN = .5
RETURN
END

SUBROUTINE WINMAX(DAT,DATMIN,DATMAX)
DIMENSION DAT(301)
DATMAX = DAT(1)
DATMIN = DAT(1)
DO 1 I = 2,301
   DATMAX = AMAX1(DATMAX,DAT(I))
1   DATMIN = AMIN1(DATMIN,DAT(I))
RETURN
END

SUBROUTINE COMPAR(CHI)
COMMON/THREE/YC(301),YCMIN,YCMAX
COMMON/FOUR/YL(301),YLMIN,YLMAX,AREAL
COMMON/FIVE/YD(301),YM0Y,YM0X
C C DO COMPARISON BETWEEN LORENTZIANS AND THEORY C
C
NP = 301
CHI = 0.
YLDIF = YLMAX - YLMIN
AREAC = 0.
DO 10 I = 1,NP
   AREAC = AREAC + (YCMAX-YC(I))
10   SCAL = AREAL/AREAC
   DO 960 I = 1,NP
      YD(I) = SCAL*(YCMAX-YC(I))
      YO(I) = (YLMAX-YL(I)) + YC(I)
   960   CHI = CHI + YD(I)**2
   CALL MINMAX(YD,YMIN,YMAX)
   PRINT 980,YMIN,YMAX,CHI
980   FORMAT(*/ MINIMUM VALUE OF RESIDUAL = * F 10.7,*
   2/ MAXIMUM VALUE OF RESIDUAL = * F 10.7,*,
   3/ FIT PARAMETER CHI = * F7.4,*)
   CALL MINMAX(YC,YCMIN,YCMAX)
   YCMIN = YCMAX - YLDIF*1.2
   RETURN
END
SUBROUTINE MOSSPLOT (DATIV, IH, I0V, IDMIDATMINOATMAX)
DIMENSION A(405), DAT(1), IN(405), IC(405), SYMBOL(6)
DIMENSION AXLAB(I1)
COMMON/TMQ/ X(301), XMIN, XMAX
DATA SYMBOL/*V*9*6*, *+/9=9*:A2, *, /
DATA BLANK/* /*
XINC = (XMAX - XMIN)/10.
AXLAB(1) = XMIN
DO 10 I = 2, I1
   ALAXAB(I) = AXLAB(I-1) * XINC
   IV = FLOAT(IV)-0.000001
   DO 2 I=1, IH3
      2 IC(I) = (TEMP - IN(I)) * 5. + 1.
   IVP = IVP + 1
   DO 3 J = 1, IVP
      3 IC(J) = SYMBOL(J)
      IF(MOD(K, IDV).EQ.1) A(I) = SYMBOL(K)
      IF(MOD(K, IDV).EQ.1) A(I) = SYMBOL(M)
      IF(MOD(K, IDV).EQ.1) A(I) = SYMBOL(I)
      K = IVP + J + 1
CONTINUE
PRINT 100, (A(L), L = 1, IH3)
RETURN
END

SUBROUTINE PLOTTER (CHI, LREN)
COMMON/ONE/PARA1(12)
COMMON/IIX/ YCF(301), YCFMIN, YCFMAX
COMMON/SEVEN/YDF(301), YDFMIN, YDFMAX
IF (LREN.EQ.0) YCFMIN = YCFMAX = (YCFMAX-YCFMIN)*1.2
PRINT 10, (PARA1(I), I = 1, 12)
FORMAT (1X, 9A, 1, 9F12.7, 9F12.7, 9F12.7)
A / x / GX = , #F12.7, x GY = , #F12.7, x GZ = , #F12.7, x
1 / x / GJ = , #F12.7, x ETA = , #F12.7, x IS = , #F12.7, x
2 / / VJ2 = , #F12.7, x WID = , #F12.7, x EQ = , #F12.7
CALL MOSSPLOT (YCF, 30, 301, 5, 10, YCFMIN, YCFMAX)
IF(LREN.EQ.0) RETURN
PRINT 980, YDFMIN, YDFMAX, CHI
980 FORMAT (1X, 1, 9F10.4)
CALL MOSSPLOT (YDF, 26, 301, 26, 10, YDFMIN, YDFMAX)
RETURN
END
SUBROUTINE FLOTDAT(X,Y,NX,YMIN,YMAX,XMIN,XMAX,NDAT,
XSIZE,YSIZE)
C PLOTDAT CREATES A PLOT OF (X,Y) DATA. THE PLOT MAY
C BE PRODUCED ON THE TEK TERMINAL OR ON THE CALCOMP
C PLOTTER BY PRECEEDING A CALL TO FLOTDAT WITH A CALL
C TO PLOTYPE. PLOTYPE HAS ONE ARGUMENT WHICH IF IT IS
C 0 - CALCOMP, 1 - TEKTERMINAL, 2 - BOTH. THERE ARE ALSO
C OPTIONS FOR PLOTTING ON A H-P PLOTTER. THE PLOT DRIVERS
C USED IN THIS PROGRAM ARE DESCRIBED IN DOCUMENTATION
C AVAILABLE THRU JEFF BALLANCE OR LARRY HUBBLE AT THE COMPUTER
C CENTER AT OSU. THE CALLING PARAMETERS FOR PLOTDAT ARE:
C
C X - ARRAY OF THE INDEPENDENT VARIABLE DATA
C Y - ARRAY OF THE DEPENDENT VARIABLE DATA
C NX - THE NUMBER OF DATA POINTS IN THE X AND Y ARRAYS TO
C BE PLOTTED.
C YMIN - MINIMUM VALUE OF THE Y-AXIS.
C YMAX - MAXIMUM VALUE OF THE Y-AXIS.
C XMIN - MINIMUM VALUE OF THE X-AXIS.
C XMAX - MAXIMUM VALUE OF THE X-AXIS.
C NDAT - INTEGER IN THE RANGE (-28,28). IF THE VALUE IS
C NEGATIVE NO LINES WILL CONNECT THE POINTS, ONLY DATA
C MARKS AT THE POINTS. IF THE VALUE IS POSITIVE LINES
C WILL CONNECT THE POINTS AND THE MARK WILL BE AT
C THE POINT.
C XSIZ - THE PHYSICAL SIZE IN INCHES OF THE X-AXIS.
C YSIZ - THE PHYSICAL SIZE IN INCHES OF THE Y-AXIS.
C
C THE PLOT BUFFER MUST BE CLEARED BY A CALL TO PLOTEND--THERE
C ARE NO PARAMETERS--AFTER A CALL TO PLOTDAT AND
C AFTER THE LABELING HAS BEEN DONE ON THE PLOT.

DIMENSION X(NX),Y(NX)
C THE SIZE ROUTINE FIXES THE BOUNDS OF THE PLOT. THE CALLING
C STRING IS:
C
C CALL SIZE(XSIZE,YSIZE)
C WHERE:
C XSIZE - SIZE IN INCHES OF THE PLOTTING AREA IN X DIR.
C YSIZE - SIZE IN INCHES OF THE PLOTTING AREA IN Y DIR.
C XSIZE = AMAX1(15.,XSIZ+5.)
C YSIZE = AMAX1(10.,YSIZ+4.)
C CALL SIZE(XSIZE,YSIZE)
C XBIAS = 3.5
C YBIAS = 2.
C
C IF THE SIZE OF THE PLOT IS SMALL ENOUGH (LESS THAN 9. X 6.5) A BOX
C WILL BE DRAWN AROUND THE PLOT
C IF(XSIZE.LE.9. AND YSIZE.LE.6.5) CALL BOX(XBIAS,YBIAS)
C
C THE SCALE ROUTINE SETS UP THE SCALE FACTORS USED IN PLOTTING.
C THE CALLING STRING IS:
C CALL SCALE(XSCAL,YSCAL,XBIAS,YBIAS,XLOW,YLOW)
C WHERE
C XSCAL - SCALE FACTOR IN X DIRECTION IN UNITS OF INCHES PER
C SCALED POINT I.E. YOUR UNITS.
C YSCAL - SCALE FACTOR IN Y DIRECTION IN UNITS OF INCHES PER
C SCALED POINT I.E. YOUR UNITS.
C XBIAS - A BIAS FACTOR IN INCHES. THIS AMOUNT WILL BE
LEFT AS A MARGIN ON THE LEFT OF PLOTTING AREA AS DEFINED
BY THE SIZE COMMAND.

YBIAS = A BIAS FACTOR IN INCHES. THIS AMOUNT WILL BE LEFT AS
A MARGIN AT THE BOTTOM OF THE PLOTTING AREA AS DEFINED
BY THE SIZE ROUTINE.

XLOW = THE LOWEST VALUE IN YOUR UNITS OF THE X-AXIS.
YLOW = THE LOWEST VALUE IN YOUR UNITS OF THE Y-AXIS.

XSCAL = XSIZE/(XMAX-XMIN)
YSCAL = YSIZE/(YMAX-YMIN)

CALL SCALE(XSIZE/(XMAX-XMIN),YSIZE/(YMAX-YMIN),XBIAS,YBIAS,
1XMIN,YMIN)

THE AXIS ROUTINE HAS PARAMETERS

CALL AXISL(XLOW,XHIGH,XORIGIN,YLOW,YHIGH,YORIGIN,XTIC,YTIC,LXTIC,LYTIC,
1LINTX,LINTY,XUNIT,YUNIT,CSIZE,XSCAL,YSCAL)

WHERE

XLOW = THE LOWEST VALUE IN YOUR UNITS OF X AXIS.
XHIGH = THE HIGHEST VALUE IN YOUR UNITS OF X-AXIS.
XORIGIN = THE CROSSING POINT ALONG THE X-AXIS OF THE Y-AXIS.
YLOW = THE LOWEST VALUE IN YOUR UNITS OF THE Y-AXIS.
YHIGH = THE HIGHEST VALUE IN YOUR UNITS OF THE Y-AXIS.
YORIGIN = THE CROSSING POINT ALONG THE Y-AXIS OF THE X-AXIS.
XTIC = THE DISTANCE IN YOUR UNITS BETWEEN MAJOR TIC MARKS
YTIC = THE DISTANCE IN YOUR UNITS BETWEEN MAJOR TIC MARKS
ALONG THE Y-AXIS.
LXTIC = NUMBER OF MINOR TIC MARKS BETWEEN EACH MAJOR TIC MARK ON
X AXIS
LYTIC = THE NUMBER OF MINOR TIC MARKS BETWEEN EACH MAJOR TIC
MARK ON THE Y AXIS
LINTX = LABELING FREQUENCY ON X AXIS
LINTY = LABELING FREQUENCY ON Y AXIS
XUNIT = SCALING VALUE FOR LABELS ON X AXIS
YUNIT = SCALING FACTOR FOR LABELS ON Y AXIS
CSIZE = SIZE OF CHARACTERS IN THE LABELS
XSCAL = AS DEFINED ABOVE
YSCAL = AS DEFINED ABOVE

NOTE

AXISL IS NOT THE ROUTINE DEFINED IN COMPLER. THE ARRANO
MANUAL. ALL BUT THE LAST TWO PARAMETERS ARE EXACTLY FROM
AXISL AS DEFINED IN THE ARRANO MANUAL. THIS VERSION WAS
WRITTEN BY SWM SINCE THE LABELING IN THE CURRENT CYBER VERSION
(29 MAR 77) WAS NOT ACCEPTABLE TO THE STANDARDS REQUESTED BY
HHW. THE LOG AXIES ARE NOT AVAILABLE IN THIS VERSION, AND
SCALING FACTORS MUST BE ENTERED IN THE PARAMETER STRING.

To determine the values for XTIC and YTIC a routine called AMARK is
used

CALL TMARK(DIF,AMARK,N)

WHERE

DIF = THE DIFFERENCE IN USERS UNITS FOR THE LENGTH OF THE AXIS
AMARK - THE DISTANCE IN USERS UNITS BETWEEN MAJOR TIC MARKS.  
   THIS WILL BE EITHER 1., 2., OR 5. TIMES A POWER OF TEN.  
   AND IS DETERMINED BY AMARK.  
N - THE MINIMUM NUMBER OF PARTS TO DIVIDE THE AXIS UP INTO.  
   THE AXIS WILL BE DIVIDED UP INTO BETWEEN N AND 2*N NUMBER OF  
   EQUAL PARTS.  

CALL TMARK(XMAX-XMIN,XTIC,10) 
CALL TMARK(YMAX-YMIN,YTIC,5) 

YHI = YMIN + (YMAX-YMIN)*.8  
CALL AXISL(XMIN,XMAX,0.,YMIN,YHI,YMIN,XTIC,YTIC,4,4,4,-1,1, 
   11.,12.,XSCAL,YSCAL) 

MARK=ABS(NOAT)  
THE ROUTINE TO PLOT IS  
CALL PLOT(X,Y,IPEN,MARK)  
WHERE  
X - X COORDINATE IN YOUR UNITS OR POINT TO PLOT TO.  
Y - Y COORDINATE IN YOUR UNITS OR POINT TO PLOT TO.  
IPEN = 0 MOVE TO POINT WITH PEN UP, 1 MOVE TO POINT WITH PEN DOWN  
MARK = AN INTEGER FROM 0 TO 28 FOR MARK TO DRAW AT THE POINT  
CALL VECTORS  
IF(NOAT.LT.0) CALL POINTS  
DO 20 I=2,NX  
CALL PLOT(X(I),Y(I),1,MARK)  
20 CONTINUE  
CALL ALPHAS  
RETURN  
END

SUBROUTINE TMARK(DIF,AMARK,N)  

THIS SUBROUTINE WILL DETERMINE THE PROPER INTERVAL FOR SPACING  
TIC MARKS ALONG AN AXIS BY BREAKING THE AXIS UP INTO BETWEEN N AND  
2*N PARTS. THE TIC MARKS WILL BE LOCATED AT POINTS WHICH ARE EITHER  
1., 2., OR 5. TIMES SOME POWER OF 10 USERS UNITS APART. THIS  
NUMBER WILL BE RETURNED AS AMARK. DIF IS THE LENGTH OF THE TOTAL  
AXIS IN USERS UNITS.  

DIMENSION JTIC(9)  
DATA JTIC/1,2,2,2,5,5,5,5,5/  
AMARK = ABS(DIF)/FLOAT(N)  
ILOG = XLOG = ALOG10(AMARK)  
IF(XLOG.LT.0.) ILOG = ILOG + 1  
IMARK = AMARK * (10.**(ILOG))  
IF (IMARK .GE.10) IMARK = 9  
IF (IMARK.LT.1) IMARK = 1  
AMARK = FLOAT(JTIC(IMARK))*10.**(ILOG)  
RETURN  
END
SUBROUTINE AXSL (XMIN, XMAX, XORG, YMIN, YMAX, YORG, XTIC, YTIC, LXTIC, LYTIC, LINTX, LINTY, XUNIT, YUNIT, CSIZE, XSCALE, YSCALE)
CALL AXIS (XMIN, XMAX, XORG, YMIN, YMAX, YORG, XTIC, YTIC, LXTIC, LYTIC, LINTX, LINTY, XUNIT, YUNIT, CSIZE)
XOFF = CSIZE*/2.*XSCALE)
YOFF = CSIZE*/2.*YSCALE
IF (LINTX) 100, 300, 200
200 XY = XTIC
XEND = XMAX
DO 290 J = 1, 2
NTIC = ABS((XEND - XORG) / XT)
IF (NTIC .LT. LINTX) GO TO 280
DO 260 I = LINTX, NTIC, LINTX
X = XORG + XT*FLOAT(I)
CALL SYMBOL (X, NPRINT, XOFF, YORG - YOFF, 0., CSIZE, NPRINT, ARRAY)
260 CONTINUE
X = -XT
XEND = XMIN
290 CONTINUE
GO TO 300
100 CALL LABELS (XMIN / XUNIT, ARRAY, NPRINT)
CALL SYMBOL (XMIN, YORG - YOFF, 0., CSIZE, NPRINT, ARRAY)
CALL LABELS (XMAX / XUNIT, ARRAY, NPRINT)
CALL SYMBOL (XMAX - 2.*NPRINT * XOFF, YORG - YOFF, 0., CSIZE, NPRINT, ARRAY)
300 CONTINUE
XOFF = XOFF * 2.
YOFF = YOFF / 4.
IF (LINTY) 400, 503, 600
600 Y = YTIC
YEND = YMAX
DO 590 J = 1, 2
NTIC = ABS ((YEND - YORG) / YT)
IF (NTIC .LT. LINTY) GO TO 580
DO 560 I = LINTY, NTIC, LINTY
Y = YORG + YT*FLOAT(I)
CALL LABELS (Y / YUNIT, ARRAY, NPRINT)
XMARK = XORG - FLOAT(NPRINT + 2) * XOFF
560 CALL SYMBOL (XMARK, Y - YOFF, 0., CSIZE, NPRINT, ARRAY)
580 Y = -YT
YEND = YMIN
590 CONTINUE
400 CALL LABELS (YMIN / YUNIT, ARRAY, NPRINT)
XMARK = XORG - FLOAT(NPRINT + 2) * XOFFF
CALL SYMBOL (XMARK, YMIN, 0., CSIZE, NPRINT, ARRAY)
CALL LABELS (YMAY / YUNIT, ARRAY, NPRINT)
XMARK = XORG - FLOAT(NPRINT + 2) * XOFFFF
CALL SYMBOL (XMARK, YMAX - 2.*YOFF, 0., CSIZE, NPRINT, ARRAY)
500 RETURN
END
SUBROUTINE LABELS (VAL, ARRAY, NPRINT)

AVAL = ABS(VAL)
IF(AVAL.GT.999.99,0R. AVAL .LT. .01) GO TO 100
N = 6
ILOG = XLOG = ALOG10(AVAL)
M = 4 - ILOG
IF(XLOG.LT.C.) M = 5
IF(VAL .LT. 0.) N = 7
NPRINT = N - M + 2
NCHAR = N
ENCODEx (6,50,FMT) N,M

50 FORMAT (*(*F$,I1g*.t.*I11*)*)
40 JJ = IFIMAVAL+.005) 100.)
IF(MOD(JJ,10).EQ.0) NPRINT = NPRINT-1
IF(MOD(JJ,100).EQ.0) NPRINT = NPRINT-2
GO TO 200
100 IF (VAL) 110.x2G,130
110 NCHAR = NPRINT = 8
FMT = 6H(E8.2)
GO TO 200
130 NCHAR = NPRINT = 7
FMT = 6H(E7.2)
20C ENCODE(NCHAR,FMT,ARRAY) VAL
RETURN
20 ARRAY = 1M0
NCHAR = NPRINT = 1
RETURN
END

SUBROUTINE BOX(XX,YY)
C THIS SUBROUTINE DRAWS AN 8.5 X 11 INCH BOX AROUND A PLOT.
C
DIMENSION CUTOUT(2)
DATA CUTOUT/20HCUT ALONG SOLID LINE/
X = XX - 1.5
Y = YY - 1.
CALL SCALE(1.,1.,X,Y,0.,0.)
CALL PLOT(0.,C.,0.,0.)
CALL PLOT(11.,0.,1.,0)
CALL PLOT(11.,8.5,1.,0)
CALL PLOT(0.,8.5,1.,0)
CALL PLOT(C.,0.,1.,0)
CALL POINTS
CALL PLOT(1.25,8.2,1,28)
CALL PLOT(5.50,8.2,1,28)
CALL PLOT(9.75,8.2,1,28)
CALL SYMBOL(4.3,8.55,0.,.12,26,CUTOUT)
RETURN
END
APPENDIX V

Program MULTEPR
Program MULTIPR(INPUT, OUTPUT, TAPE61=OUTPUT, TAPE10)

This program computes the polycrystalline absorption pattern for the following system:

- **Spin**: 1/2
- **G-Tensor**: GX, GY, GZ
- **RF**: Microwave frequency (in GHz)
- **GAM**: Width at half-maximum of Lorentz line
- **RF**: Microwave frequency (in GHz)
- **GAM**: Width at half-maximum of Lorentz line
- **(Lorentz lineshape assumed)**
- **WL**: Lower field limit (in Koe)
- **MU**: Upper field limit (in Koe)
- **NSPEC**: Number of spectra to be simulated
- **NB**: Number of theta points
- **NC**: Number of psi points
- **NPOINTS**: Number of data points for spectrum plot
- **XLENGTH**: Length of X axis in inches (default = 10)
- **YLENGTH**: Length of Y axis in inches (default = 6)
- **CHARSZ**: Height of characters on plot (default = .12)
- **SP**: Absorption spectrum
- **OSP**: Derivative spectrum
- **OSPTOT**: Total derivative spectrum (ACD mixture)
- **NCOMP**: Number of components for a given spectra
- **NSET**: Number of sets of weighting factors to be read in
- **WT**: Weighting factor given to each component of spectra
- **IFLOT**: Defines plotter to be used. If IFLOT = 0, Calcomp plotter is used. If IFLOT = 3, the Gerber plotter is used.

This program allows add mixtures of spectra to be calculated. If more than one spectra is to be mixed, NCOMP is set to the number of component spectra to be added together. Each component is weighted by the weighting factor WT. There will be one weighting factor for each component. WT(1) will be associated with the first component, WT(2) with the second, etc.

One spectra is defined as having NSPEC components. Thus if three one component spectra are to be calculated, NSPEC = 3, and NCOMP = 1 for each spectra. If two three component spectra are to be calculated NSPEC = 2, and NCOMP = 3 for each spectra. If NCOMP is greater than 1 (a multi component spectra), weighting factors are read in and the NCOMP components of the spectra are weighted and added together. Several different mixing ratios of one spectra can then be calculated.

If NB or NC are to be determined internally (set to zero on input), the following formula is used:

\[ NB(OR NC) = 6 \times \left( \frac{\text{const} \times RF \times (1/AMIN1(G)) - (1/AMAX1(G))) + GAM}{GAM} \right) \]

Where G = GX, GY, GZ

Euler angles from Rutherford... physical rotations so there are negative angles in each of Rutherford's simple rotations.
MATRICES

PSI IS THE FIRST ROTATION ANGLE, THETA IS THE SECOND, AND PHI IS THE THIRD. PHYSICAL ROTATION OF G-TENSOR UTILIZES PSI AND THETA. PHYSICAL ROTATION OF A UNIT VECTOR HRF ORIGINALLY IN Z-DIRECTION TO ORIENTATION IN XY PLANE ACCOMPLISHED BY THE PSI=E*, THETA=90*, AND PHI=ARBITRARY NUMBER.

RUTHERFORD CALLS HIS FIRST ROTATION ANGLE PHI. HENCE

PHI(RUTHERFORD) = PSI(HHW)

THE METHOD USED IS TO FIX THE EXTERNAL POLARIZING FIELD, H0, ALONG THE Z-AXIS, AND THE MICROWAVE FIELD ALONG THE X-AXIS. THE POLYCRYSTALLINE PATTERN IS SIMULATED BY PHYSICAL ROTATIONS OF THE G-TENSOR TO A RANDOM SET OF ORIENTATIONS.

FOR EACH G-TENSOR ORIENTATION THE MICROWAVE FIELD IS ROTATED THROUGH 90 DEGREES TO SIMULATE A POWDER PATTERN.

INPUT PARAMETERS

CARD 1 (I16,3F10.5,I10)

COLUMN

1 - 10 NSPEC
11 - 20 XLENGTH (DEFAULT = 10.)
21 - 30 YLENGTH (DEFAULT = 5.)
31 - 40 CHARSZ (DEFAULT = .12)
41 - 50 IPlot

CARD 2 (3E10.4,2I5) REPEAT NSPEC TIMES

COLUMN

1 - 10 RF
11 - 20 HL
21 - 30 HU
31 - 35 NPOINTS (DEFAULT = 201)
36 - 40 NCOMP (DEFAULT = 1)

CARD 3 (4E10.4,2I5)

COLUMN

1 - 10 GX
11 - 20 GY
21 - 30 GZ
31 - 40 GAM
41 - 45 NB (DEFAULT CALCULATED FROM PARAMETERS)
46 - 50 NC (DEFAULT CALCULATED FROM PARAMETERS)

CARD 4 (I5)

COLUMN

1 - 5 NSET

CARD 5 (10F8.0)

COLUMN

1 - 8 WT(1)
9 - 16 WT(2)
17 - 24 WT(3)
25 - 32 WT(4)
THE FOLLOWING FLOW CHART WILL SHOW THE FLOW OF THE PROGRAM AND
SERVE AS A GUIDE IN SETTING UP AN INPUT DECK.

START

READ IN CARD 1 AND ASSIGN DEFAULT VALUES FOR PARAMETERS WHICH ARE ZERO

SET ISPEC = 1 AND USE AS A DO LOOP COUNTER

READ CARD 2 AND ASSIGN DEFAULT VALUES

SET ICOMP = 1 AND USE AS A DO LOOP COUNTER

READ CARD 3 AND ASSIGN DEFAULT VALUES

CALCULATE THE ICOMP COMPONENT OF THE ISPEC SPECTRA AND PLOT IT

INCREMENT ICOMP AND CHECK IF GREATER THAN NCOMP

IF NCOMP EQUALS 1 GO TO (A)

READ IN CARD 4 SET ISET = 1 AND USE AS A DO LOOP COUNTER

READ CARD 5 AND OBTAIN WEIGHTING FACTORS FOR EACH COMPONENT. WT(1) BEING THE WEIGHTING FACTOR FOR THE ICOMP = 1 COMPONENT, ETC.
CALCULATE THE TOTAL SPECTRA FROM ADD MIXTURES AND PLOT IT

INCREMENT ISET AND CHECK IF ISET > NSET

INCREMENT ISPEC AND CHECK IF ISPEC > NSPEC

DIMENSION SP(512),X(512),DSP(512,10),DSPTOT(512),WT(10)
DIMENSION ARRAY(9),TITLE(3)
REAL IX,IY,IZ
DATA XOFF/3.,YOFF/3./
DATA (TITLE = 'MAGNETIC FIELD IN KOE')
PI = 4. * ATAN(1.)
CONST = 6.62554E-18 / 92731 E-17

CONST = PLANCK'S CONST / BETA IN UNITS OF KOE SEC

READ IN NUMBER OF SPECTRA TO BE SIMULATED AND NUMBER OF DATA POINTS

WRITE (61,25)
25 FORMAT (*1$)
READ 10,NSPEC,XLENGTH,YLENGTH,CHARSZ,IPILOT
10 FORMAT(I10.3F10.5,I10)

ASSIGN DEFAULT VALUES FOR PLOT PARAMETERS

IF (XLENGTH.EQ.0.) XLENGTH = 10.
IF (YLENGTH.EQ.0.) YLENGTH = 6.
IF (CHARSZ.EQ.0.) CHARSZ = 12
CALL PLOTYPE (IPILOT)
CALL PLCILUN(10)
CALL SIZE (1.5*XLENGTH + XOFF,1.5*YLENGTH + YOFF)

LOOP ON NSPEC

DO 1010 ISPEC=1,NSPEC

READ IN CARO TYPE 2 AND ASSIGN DEFAULT VALUES

READ 15,RH,HL,HU,NPOINTS,NCOMP
15 FORMAT (3E10.4,2I5)
IF (NPOINTS.EQ.0.) NPOINTS = 201
IF (NCOMP.EQ.0) NCOMP = 1

USE HL, HU, AND NPOINTS TO CALCULATE THE X-AXIS

HDIF = HU - HL
MMID = HL + HDIF/2.
DELH = HDIF/FLOAT(NPOINTS - 1)
X(I) = HL
DO 110 I=2,NPOINTS
110 X(I) = X(I-1) + DELH

LOOP ON NCOMP THEN

READ IN PARAMETERS CHARACTERIZING THE ICOMP COMPONENT OF A SPECTRA CARD TYPE 3

DO 2000 ICOMP = 1,NCOMP
READ 20,GX,GY,GZ,GAM,NB,NC
20 FORMAT (4E10.4,215)

CALCULATE THE FEWEST NUMBER OF POINTS NECESSARY FOR A GOOD SPECTRA AS DESCRIBED EARLIER AND ASSIGN IT TO NB OR NC AS PRE DEFAULT REQUIREMENTS

OPTIMAL = (1./AMIN1(GX,GY,GZ))-(1./AMAX1(GX,GY,GZ))
NOPT = (OPTIMAL * RF * CONST + GAM) * 6./GAM
IF(NB.EQ.0) NB = NOPT
IF(NC.EQ.0) NC = NOPT

PRINT OUT SPECTRA PARAMETERS ON LINE PRINTER SO THE USER KNOWS WHAT HE REQUESTED.

PRINT 21, ISPEC,ICOMP,GX,GY,GZ,NB,NC,RF,GAM,HL,HU,NPOINTS
21 FORMAT (2 SPECTRA SIMULATED... 5 IS/5 COMPONENT ... 5 5 5 5
E/,3GX #,T10,==E12.5/# GY#,T10,==E12.5/# HU#,T10,==E12.5/# NPOINTS#,T10,==E12.5/# 5 5 5 5 5 5

ZERO OUT ABSORPTION SPECTRA

DO 108 I=1,NPOINTS
108 SP(I)=0.

BEGIN LOOPS ON THETA (NB) AND PSI (NC) TO SAMPLE POSSIBLE EFFECTIVE G-VALUES

XA = X9 = XC = 0.
IF (NB.NE.1) X9=(PI/2.*FLOAT(NB-1))
IF (NC.NE.1) XC=(PI/2.*FLOAT(NC-1))
A = B = C = 0.
GGX = GX * GX
GGY = GY * GY
GGZ = GZ * GZ
DO 900 IC = 1,NC
SC = SIN (C)
CC = COS (C)
CC2 = CC * CC
C SC2 = SC * SC
DO 800 IB = 1,NB
C
C COMPUTE GEFF AND H FOR A GIVEN PSI(C) AND THETA(B).
C
CB = COS (B)
SB = SIN (B)
SB2 = SB * SB
CB2 = CB * CB
G1 = GX * SB * CC
G2 = GY * SB * SC
G3 = GZ * CB
GEFF2 = (G1**2 + G2**2 + G3**2)
GEFF = SQRT(GEFF2)
HO = CONST * RF/GEFF
HI = (GGX*GGY*SB2+GGY*GGZ*(SC2+CB2*CC2)+GGZ*GGX*(CC2+
1*CB2*SC2)) / (2.*GEFF2)
HI = SORT(HI)*SB
A = 0.
B = B + XB

C SUM UP LCORENTZ ABSORPTION PEAKS AT RESONANCE FIELDS
C
DO 115 I=1,NPOINTS
SP(I) = SP(I) +FL(X(I),HO,H1,GAM)
115 CONTINUE

C CONTINUE

B = 0.
C = C + XC
980 CONTINUE

C NORMALIZE THE AREA UNDER THE CURVE TO ONE USING THE
C TRAPEZIOD RULE
C
CALL NORMAL (SF,NPOINTS)

C CALCULATE DERIVATIVE OF SPECTRUM
C
DELH2 = 2. * DEH
NPNTS1 = NPNTS - 1
DO 99 I=2,NPNTS1
DSP(I,ICOMP) = (SP(I+1) - SP(I-1))/DELH2
99 CONTINUE
DSP(I,ICOMP) = DSP(2,ICOMP)
DSP(NPNTS,ICOMP) = DSP(NPNTS1,ICOMP)

C PLOT SPECTRUM
CALL BOX(XOFF,YOFF,XLENGTH,YLENGTH)

C AUTOSCALE THE DATA
C
195 SPDMIN = SPMAX = 0.
DO 201 I=1,NPOINTS
201 IF (SP(I).GT.SPMAX) SPMAX=SP(I)
C
SPDF = SPMAX - SPDMIN
SPMIN = SPMIN - SPDIFF/2.
SPMAX = SPMAX + SPDIFF/2.
SPDIFF = SPDIFF * 2.
XSCAL = LENGTH/HDIF
YSCAL = LENGTH/SPDIFF
CALL SCALE (XSCAL,YSCAL,XOFF,YOFF,ML,SPMIN)

C DRAW THE AXIS
CALL AXIS (HL,HU,SPMIN,SPMAX,SPMIN,HDIF/10.,0.,1.,0)

C LABEL THE X-AXIS
CALL AXIS (HL,HU,HU,SPMIN,SPMAX,SPMIN,HDIF/10.,0.,1.,0)
XXOFF = 3. * CHARSZ/XSCAL
YXOFF = 2. * CHARSZ/YSCAL
ENCODER (6,202,ARRAY) HL

C PLOT THE DATA
HF = HL
CALL PLOT (HF,SP(1),0,0)
DO 203 I=1,NPOINTS

C IN ORDER FOR THE PLOT TO LOOK NICE AND KEEP COSTS DOWN, THE
SPECTRA IS PLOTTED AS A DOTTED LINE.

IPEN = MOD(I,3)
CALL PLOT (HF,SP(I),IPEN)

C PLOT DSP SPECTRUM
DSMIN=DSPMAX=0.
DO 90 I=1,NPOINTS
IF (CSP(I,ICOMP).LT.DSPMIN) DSPMIN = DSP(I,ICOMP)
90 IF (CSP(I,ICOMP).GT.DSPMAX) DSPMAX = DSP(I,ICOMP)
DSPDEL = DSPMAX - DSPMIN
DSPMIN = DSPMIN - DSPDEL/2.
DSPDEL = DSPDEL * 2.
YSCAL = LENGTH/DSPDEL
CALL SCALE (XSCAL, YSCAL, XOFF, YOFF, HL, DSPMIN)
HF = HL
CALL PLOT (HL, DSP(I, ICOMP), 0, 0)
DO 91 I = 1, NPOINTS
CALL PLOT (HF, DSP(I, ICOMP), 1, 0)
91 HF = HF + DELH
2000 CALL PLOTEND
IF (NCOMP.LT.1) GO TO 1310
READ 400, NSET
400 FORMAT(I5)
READ 410, MT
410 FORMAT(10F8.0)
DO 430 I = 1, NPOINTS
TOT = 0.
DO 420 J = 1, NCOMP
420 TOT = TOT + WT(J) * DSP(I, J)
430 DSPTOT(I) = TOT
CALL BOX(XOFF, YOFF, XLENGTH, YLENGTH)
C PLOT DSPTOT SPECTRUM
C DSPMIN = DSPMAX = 0.
DO 39 I = 1, NPOINTS
39 IF (DSPTOT(I) .LT. DSPMIN) DSPMIN = DSPTOT(I)
IF (DSPTOT(I) .GT. DSPMAX) DSPMAX = DSPTOT(I)
DSPDEL = DSPMAX - DSPMIN
DSPMIN = DSPMIN - DSPDEL/2.
DSPDEL = DSPDEL * 2.
DSPMAX = DSPMIN + DSPDEL
YSCAL = YLENGTH/DSPDEL
YXOFF = 2. * CHARSZ/YSCAL
CALL SCALE (XSCAL, YSCAL, XOFF, YOFF, HL, DSPMIN)
C DRAW THE AXIS
C CALL AXIS (HL, MU, HL, DSPMIN, DSPMAX, DSPMIN, HDIF/10., 0., 1., 0)
C LABEL THE X-AXIS
C CALL AXIS (HL, MU, HL, DSPMIN, DSPMAX, DSPMIN, HDIF/10., 0., 1., 0)
C XXOFF = 3. * CHARSZ/XSCAL
C YYOFF = 2. * CHARSZ/YSCAL
C ENCODE (6, 202, ARRAY) HL
C CALL SYMBOL (HL-XOFF, DSPMIN-YXOFF, 0., CHARSZ, 6, ARRAY)
C ENCODE (6, 202, ARRAY) MU
C CALL SYMBOL (MU-XXOFF, DSPMIN-YXOFF, 0., CHARSZ, 6, ARRAY)
C CALL SYMBOL (HMID-3.5*XXOFF, DSPMIN-2.*YYOFF, 0., CHARSZ, 21, 1 TITLE)
C
C THE FOLLOWING CODE PUTS THE WEIGHTING FACTORS ON THE TOP OF THE COMPOSITE SPECTRA. SINCE THERE ARE UP TO 13 WEIGHTING FACTORS AND ROCM FCR ONLY FIVE ACROSS, THE FOLLOWING CODE CHECKS FOR THE NUMBER OF LINES NECESSARY AND CALLS THAT JJ. THE NUMBER OF WEIGHTING FACTORS ON ONE LINS IS GIVEN BY NTIME.
C

JJ = FLOAT(NCOMP)/5. + .9
DO 510 J = 1, JJ
NTIME = MINC(5, NCOMP - 5*(J-1))
NCHAR = 16 * NTIME
J1 = (J-1) * 5
NCOUNT = J1 + NTIME
J1 = J1 + 1

CODE UP ONE OR TWO LINES, WHERE NCOUNT IS THE NUMBER PER LINE

ENCODENCHAR, 502, ARRAY) NTIME, (I,WT(I), I=J1, NCOUNT)
502 FORMAT(*)
51C CALL SYMBOL (HMID, 2.667*NTIME*XXOFF, DSPMAX - J*YXOFF, 0., CHARSZ, 1, NCHAR, ARRAY)

PLOT DATA NOW

HF = HL
CALL PLOT (HL, DSPTOT(I), 1, 0)
DO 41 I = 1, NPOINTS
CALL PLOT (HF, DSPTOT(I), 1, 0)
41 HF = HF + DELH
CALL PLOTEND
1000 CONTINUE
1010 CONTINUE
END

SUBROUTINE BOX(X, Y, XL, YL)
DIMENSION CUTOUT(2)
DATA CUTOUT /2CHCUT ALONG SOLID LINE/
CALL VECTORS
IF(XL.GT.10., OR, YL.GT.7.) RETURN
XX = X - (11. - XL)/2.
YY = Y - (8. - YL)/2.
CALL SCALE (1., 1.*XX, YY, 0., 0.)
CALL FLOT (0., 0., 0., 0.)
CALL FLOT (11., 0., 1., 0.)
CALL FLOT (11., 8.5, 1., 0.)
CALL FLOT (0., 8.5, 1., 0.)
CALL FLOT (0., 0., 0., 0.)
CALL POINTS
CALL FLOT (1.25, 4.2, 1.28)
CALL FLOT (5.56, 5.2, 1.28)
CALL FLOT (9.75, 8.2, 1.28)
CALL SYMBOL (4.3, 8.55, 0., 12.20, CUTOUT)
CALL VECTORS
RETURN
END
FUNCTION FL(X,W,H1,G)
FL = (X-1)/(4.*((X-W)/G)**2 + 1.)
RETURN
END

SUBROUTINE NORMAL(SP,NPTS)
DIMENSION SP(512)
NP1 = NPTS - 1
AREA = 0.
DO 10 I = 2,NP1
    AREA = AREA + SP(I)
    AREA = AREA + (SP(I) + SP(NPTS))/2.
10    DO 20 I = 1,NPTS
20    SP(I) = SP(I)/AREA
RETURN
END
APPENDIX VI

Program MOSSFIT
PROGRAM MOSSFIT (INPUT,OUTPUT,PUNCH,TAPE61=OUTPUT,TAPE10)

MOSSFIT USES THE BELL LABS VERSION OF NLLSQ MODIFIED TO RUN
ON A CYBER 73 COMPUTER. THE USER IS REFERRED TO THE WRITE-UP
ON THE ORIGINAL PROGRAM BEFORE MAKING ANY CHANGES IN THE
REQUESTED OUTPUT OR OPTIONS.

INPUT PARAMETERS:

- \( 8 \) = THE ARRAY CONTAINING THE INPUT PARAMETERS FOR THE FIT
- \( KITER \) = THE NUMBER OF ITERATIONS TO USE IN FITTING
  IF \( KITER > 99 \), THE PROGRAM STOPS.
- \( NP\text{PAIR} \) = THE NUMBER OF PAIRS OF PEAKS TO BE FIT.
- \( NS\text{ING} \) = THE NUMBER OF SINGLE PEAKS TO BE FIT
- \( N\text{PLT} \) = FLAG FOR PLOTTING OF DATA AND FITTED CURVE.
  IF \( N\text{PLT} \) IS POSITIVE, THE PLOT WILL BE DONE ON THE
  CALCOMP PLOTTER. IF ZERO, NO PLOT.
  IF \( N\text{PLT} \) IS NEGATIVE THE PLOT IS DONE ON THE GERBER.
- \( NC\text{AL} \) = FITTING FLAG FOR CALIBRATIONS IF \( NC\text{AL} \) NE 0
  CALIBRATION CONSTANTS ARE CALCULATED
- \( T\text{ITLE} \) = A TITLE FOR THE RUN (FURNISHED BY MOSSRED).
- \( Y\text{MAX}, Y\text{MIN}, N\text{PTS}, \text{AND NOEL} \) ARE SCALING INFORMATION USED IN
  PLOTTING
- \( V\text{ELC} \) AND \( CG \) ARE THE CALIBRATION CONSTANTS FOR THE SPECTRA
  \( X \), AND \( Y \) ARE THE DATA ARRAYS

This program fits a mOssbauer spectra of intensity (relative)
As a function of channel number. The model used is Lorentzian.
The peaks are either specified as single peaks, characterized
by an intensity or height, a full width at half maximum, and a
position; or as pairs of peaks, characterized by a height, full width
at half maximum, position of the first peak, position of the second
peak, and a ratio, where \( \text{Ratio} = H1/H2 \). The height and full
width at half max for the second peak is calculated from the
height and width of the first peak, assuming the area under both
peaks is the same. Thus:

- \( H2 = H1/\text{Ratio} \)
- \( G2 = G1 \times \text{Ratio} \)

Where

- \( H1 \) AND \( H2 \) ARE THE HEIGHTS OF THE FIRST AND SECOND
  PEAKS RESPECTIVELY. \( G1 \) AND \( G2 \) ARE THE FULL WIDTH
  AT HALF MAXIMUM FOR THE FIRST AND SECOND PEAKS
  RESPECTIVELY.

Thus we can see that \( H2 = H1/\text{Ratio} \) = \( H1 \times G1 \)
AND HENCE THE PEAKS HAVE THE SAME AREA. THE UNITS OF HEIGHT ARE
RELATIVE INTENSITY UNITS, THE OTHER PARAMETERS ARE IN UNITS
OF CHANNELS. THE HEIGHT OF THE PEAKS IS THE INTENSITY
UNITS DOWN FROM A BASELINE OR BACKGROUND WHICH MUST ALSO
BE SPECIFIED. IF \( \text{Ratio} \) IS SET TO ZERO FOR THE PAIRS OF PEAKS
THE DEFAULT VALUE OF -1 IS USED. THAT IS, THE RATIO IS HELD
FIXED AT 1. HOLDING VALUES CONSTANT WILL BE DISCUSSED LATER.

To determine the calibration constants for an iron foil calibration
SET \( NC\text{AL} \) NON-ZERO AND SPECIFY THE PEAKS AS PEAK PAIRS WITH SPLITTINGS
GOING FROM LARGEST TO SMALLEST. IF 3 PEAK PAIRS ARE PRESENT, THE
PROGRAM ASSUMES THAT THE 10.657 MM/SEC PAIR IS FIRST PAIR SPECIFIED
IN DETERMINING THE CG AND VELC, THE RELATIVE INTENSITIES OF THE PEAK
PAIRS ARE USED AS WEIGHTING FACTORS.

THE INPUT CARD TYPES READ CONTAIN THE FOLLOWING:

CARD 1:
  KITER, NPAIR, NSING, NPLT, NCAL
  (5I5)

CARD 2:
  BACKGROUND IN RELATIVE INTENSITY UNITS
  (F10.5)

CARD 3:
  HEIGHT, HALF-WIDTH, POSITION(1), POSITION(2), AND RATIO
  (5F10.5)

CARD 4:
  SAME AS CARD 3
  THIS IS REPEATED UNTIL ALL PAIRS OF PEAKS ARE CHARACTERIZED
  IF THERE ARE NO PAIRS OF PEAKS, THIS GROUP IS OMITTED.

CARD 5:
  HEIGHT, HALF-WIDTH, AND POSITION
  (3F10.5)

CARD 6:
  SAME AS CARD 5
  THIS IS REPEATED UNTIL ALL SINGLE PEAKS ARE CHARACTERIZED
  IF THERE ARE NO SINGLE PEAKS, THIS GROUP IS OMITTED.

CARD 7:
  TITLE
  (10A8)
  THIS CARD IS PROVIDED BY MOSSRED

CARD 8:
  YMAX, YMIN, CG, VELC, NPTS, NDEL
  (*F10.5, 2I5)
  THIS CARD IS PROVIDED BY MOSSRED

CARDS 9-A:
  (X(K), Y(K), K=1,NPTS)
  (6(F4.0, F8.4))
  THE DATA DECK AS PUNCHED BY MOSSRED

TO RUN THE PROGRAM THE FOLLOWING INFORMATION SHOULD BE
NOTED. SINGLE PEAKS ARE SPECIFIED AFTER PAIRS OF PEAKS.
FURTHER, IF ONLY PAIRS OF PEAKS ARE USED FOR THE MODEL, CARDS
FOR SINGLE PEAKS ARE OMITTED, AND IF ONLY SINGLE
PEAKS ARE USED, CARDS FOR PAIRS OF PEAKS ARE OMITTED.

EXAMPLE 1:  FOR MODEL WITH 3 PAIRS OF PEAKS, THE FOLLOWING
CARD TYPES ARE NEEDED:
EXAMPLE 2: FOR MODEL WITH 4 SINGLE PEAKS, THE FOLLOWING CARD TYPES ARE NEEDED:
1,2,3,3,3,37,8,9,1(WITH KITER > 99)

EXAMPLE 3: FOR MODEL WITH 2 PAIRS OF PEAKS AND 3 SINGLE PEAKS, THE FOLLOWING CARD TYPES ARE NEEDED:
1,2,3,3,3,5,5,7,8,9,1(WITH KITER > 99)

IF MORE THAN ONE DECK IS TO BE FIT IN THE SAME RUN, THE DECK STRUCTURE REQUIRED FOR THE SECOND RUN SIMPLY FOLLOWS THE FIRST.

OUTPUT

THE PROGRAM GENERATES PUNCH, LINE PRINTER AND PLOT OUTPUT AS FOLLOWS:

PUNCH:
CARD 1: BKG
      (F10.5)
CARD 2-N: HEIGHT, HALF-WIDTH, AND POSITION
      (3F10.5)
THERE WILL BE ONE CARD FOR EACH PEAK

LINE PRINTER:
INTERMEDIATE OUTPUT AS SPECIFIED BY NARRAY(5)
FINAL OUTPUT AS SPECIFIED BY NARRAY(6), EXCEPT THAT
THE DATA AND CALCULATED MODEL ARE NOT PRINTED DUE TO A
GO TO STATEMENT IN THE SUBROUTINE NLLSQ. THE REMAINING
PRINT CUT GIVES THE TITLE, FINAL FITTED PARAMETERS, AND
THE INITIAL ESTIMATES FOR ALL PEAKS.

PLOTTER:
PLOT OUTPUT CONTAINS THE INITIAL DATA,
THE FINAL MODEL, THE PARAMETERS FOR EACH PEAK, THE
BACKGROUND, AND VERTICAL LINES DRAWN TO INDICATE
THE HEIGHT AND POSITION OF EACH PEAK.
IF CALIBRATION INFO IS AVAILABLE, THE CG AND VELC
ARE PRINTED ON THE PLOT, A VELOCITY AXIS IS DRAWN
THE PARAMETERS GAMMA AND POSITION ARE GIVEN IN UNITS
OF MM/SEC.
A SEPARATE PLOT OF THE RESIDUALS IS ALSO PLOTTED.

ONE OPTION OF THIS PROGRAM ALLOWS THE USER TO HOLD ANY
PARAMETER OR PARAMETERS FIXED FOR THE RUN. THIS IS DONE BY GIVING THE
PARAMETER A NEGATIVE VALUE. THE NEGATIVE VALUE SETS A FLAG TO
HOLD THE PARAMETER FIXED AND THE ABSOLUTE VALUE OF THE TERM IS
THEN SUBSTITUTED FOR IT.

ADDITIONAL ARRAYS USED IN THE PROGRAM:
BB = THE INITIAL PARAMETERS FOR PRINTING
A = THE PEAK PARAMETERS AS SINGLE PEAKS ONLY
FOR USE IN PLOTTING
RES = RESIDUAL ARRAY FROM NLLSQ
NARRAY, ARRAY ARE ARRAY ARE PARAMETERS FOR NLLSQ AND
EXPLAINED IN THE WRITE UP FOR THE SUBROUTINE
IB = THE INDEXES OF THE PARAMETERS TO BE HELD CONSTANT

DECK STRUCTURE:
THE FOLLOWING CONTROL CARDS MUST BE USED FOR THE CYBER VERSION.
IF NO PLOTTING IS TO BE DONE, THE LABEL CARD SHOULD BE OMITTED.

USER,50350,ABCD.  (REPLACE ABCD WITH APPROPRIATE USER CODE.)
CHARGE,725160,A.
SETTL,500.
LDBL,TAPE10,VSN=13014,LM=KU,F=S,FO=W,PM=ABCD.
(USE WHAT EVER IS APPROPRIATE FOR VSN = , AND PM = )
REWIND,TAPE10.*
GET,FITBIN.
ATTACH,COMPLLOT/UN=LIBRARY.
LDSET,LIB=COMPLLOT.
FITBIN.
REWIND,TAPE10.
7/8/9

DATA DECK AS PREVIOUSLY DESCRIBED

7/8/9

THIS PRESUPPOSES THAT THE BINARY DECK FOR THIS PROGRAM
IS ON THE PERMANENT FILE FITBIN. TO CREATE THAT FILE USE:

USER,50350,ABCD.  (REPLACE ABCD WITH APPROPRIATE USER CODE.)
CHARGE,725160,A.
SETTL,500.
FTN,B=FITBIN.
SAVE,FITBIN.
7/8/9

FORTRAN DECK OF MOSSFIT

7/8/9

IF THE BINARY FILE DOES NOT EXIST BUT A BINARY DECK DOES, THE
BINARY FILE MAY BE CREATED BY THE FOLLOWING:

USER,50350,ABCD.  (REPLACE ABCD WITH APPROPRIATE USER CODE.)
CHARGE,725160,A.
SETTL,500.
COPYBF,INPUT,FITBIN.
7/8/9

BINARY DECK OF MOSSFIT

7/8/9

6/7/9

6/7/9
TO RUN THE PLOT FROM THE TAPE CREATED BY MOSSFIT, THE FOLLOWING
OS-3 DECK MUST BE RUN. SEE COMP CENTER NEWSLETTER VOL XI, NO. 4, PAGE 5.
(NOTE THAT IN THE FOLLOWING THE SYMBOL ( ) REPRESENTS THE OS-3 CONTROL PUNCH)

[JOB,M1,172516C, SAVE FOR WICKMAN
[EQUIF,1=MT,13014, AT 800, PW=ABCD
[TIME=200
[MPBLK5=400
[REWIND=1
[EQUIP,2=PLOT
[LABEL,2=WICKMAN
[COPY,1=1,0=2,P=0
[REWIND,1
[LOGOFF

------------------------------------------------------------------

IF THE GERBER PLOTTER IS USED, MODIFY THE DECK STRUCTURE
ACCORDING TO THE CYBER COMPLOT MANUAL
------------------------------------------------------------------

DIMENSION X(512), Y(512), 8(45)
DIMENSION A(90)
DIMENSION BB(45)
DIMENSION TITLE(10)
DIMENSION ARRAY(8), ARRAY(8), IB(45), RES(512), FMT(10)
COMMON /DATA5/ NPAIR, NPAIR, NSING
NPLOT = 0
PI02 = 2. * ATAN(1)

C READ IN FITTING INFORMATION
10 READ 10, KITER, NPAIR, NSING, NPLT, NCAL
 FORMAT (5IS5)
 IF (KITER.GT.99) GO TO 901
 NTOT=1

C READ IN BACKGROUND

30 READ 30, B(I)
 FORMAT (5F10.5)

C READ IN PARAMETERS FOR PAIRS OF PEAKS IN NPAIR > 0

40 IF (NPAIR) .LE. 60
 NTOT=NTOT+5*NPAIR
 DO 50 I=2, NTOT+5
 NSUB=I+4
 READ 35, B(IJ), J=1, NSUB

C SET RATIO TO -1 IF RATIO IS LEFT BLANK OR SET TO ZERO
C NOTE THAT IF THE FIELD IS LEFT BLANK, ZERO IS ASSUMED BY THE
C COMPUTER
C IF(NSUB).EQ.0.) B(NSUB) = -1.
50 CONTINUE
C
C READ IN PARAMETERS FOR SINGLE PEAKS IF NSING > 0
C
60 IF (NSING) 70,90
70 NL=NTOT+1
NTOT=NTOT+3*NSING
DO 80 I=NL,NTOT,3
NSUB=I+2
READ 30,(B(J),J=I,NSUB)
80 CONTINUE
C
C READ IN DECK PRODUCED BY MOSSRED
C
90 READ 15, TITLE
15 FORMAT(10A8)
READ 20,YMAX,YMIN,CG,VELC,NPTS,NOEL
20 FORMAT (4F10.5,2I5)
READ 100,(X(K),Y(K),K=1,NPTS)
100 FORMAT (6(F4.0,F8.4))
C
C CHECK FOR ANY PARAMETERS BEING HELD CONSTANT
C
IP=0
DO 105 I=1,NTOT
IF (B(I).GE.0.) GO TO 105
IP=IP + 1
IB(IP) = I
B(I)=ABS(B(I))
105 BB(IP)=B(I)
C
C SET UP CONSTANTS FOR THE FIT
C
NARRAY(1) = NPTS - NOEL
NARRAY(2) = 1
NARRAY(3) = NTOT
NARRAY(4) = IP
NARRAY(5) = 1
NARRAY(6) = 1
NARRAY(7) = 61
NARRAY(8) = KITER
NOEL = NOEL + 1
DO 106 I=1,8
106 ARRAY(I)=0.
ENCOD (69,110,FMT) TITLE
110 FORMAT (6(I9.6,F8.4),13A8,4X)
CALL NLLSQ (Y(NOEL),X(NOEL),B,RES(NOEL),NARRAY,ARRAY,IB,FMT)
IF (NCAL.EQ.3) CALL CALIB(B,NOFAIR,CG,VELC)
C
C START PRINT OUT AND PUNCH OUT
C ARRAYS AT THIS POINT CONTAIN:
C BB IS INITIAL PARAMETERS
C B ARE FINAL PARAMETERS
C
NTOT = 1
193

73/74  OPT=1 TRACE  FTN 4.6*452

PRINT 107, TITLE
107 FORMAT (1H1,13*(1H*),/23X,1GA8
1,//,4X,*FINAL (AND INITIAL) FITTING PARAMETERS FROM NLLSO#  
2,//,1X,13*(1H*))
PUNCH 15,TITLE
IF (VELC.NE.0.) PRINT 108,VELC,CG
108 FORMAT (//,5X, VeLC = 2, G14.7, # MM/SEC/CH#, 5X, #CG = 2, G14.7, # CH#)
PUNCH 129,B(1),B(1)

120 FORMAT (//,# 5X, BACKGROUND = 2, G14.7, # (-,G14.7, #))
PUNCH 200,B(1)
A(1) = B(1)
KK = 2
IF (NPAIR) 130,150

130 PRINT 140,NPAIR
140 FORMAT (420
FOR THE 2122 PAIRS OF PEAKS THE PARAMETERS#  
1# ARE# = 2, 1H0, 13X, #HEIGHT#25X, #HALF-WIDTH#25X, #POSITION#  
225X, # MT1/MT2 # X/)
NTOT=NTOT+5*NPAIR
DO 145 I=2,NTOT,5
A(KK) = B(I) 
$ A(KK+1) = B(I+1)  \$  A(KK+2) = B(I+2) 
KK = KK+3
NSUB=I+2
PRINT 299, (B(J), B(J), J=I,NSUB), B(I+4), B(I+4)
PUNCH 200,B(I),B(I+1),B(I+2)
R = B(I+4)
AREA = P02*B(I+1) * B(I)
RR = B(I+4)
A(KK) = 3(I)/R 
$ A(KK+1) = 9(I+1)*R  \$  A(KK+2) = B(I+3)
BB(I+1) = BB(I+1)*RR 
$ BB(I+1) = BB(I+1)*RR  \$
PUNCH 295, A(KK), BB(I), BB(I+1), BB(I+2), AREA
PRINT 295, A(KK), BB(I), BB(I+1), BB(I+2), AREA
KK = KK+3

145 CONTINUE
150 IF (NSING) 160,190

160 PRINT 170,NSING

170 FORMAT(420
FOR THE 2122 SINGLE PEAKS, THE #  
1# PARAMETERS ARE# = 2, 1H0, 13X, #HEIGHT#25X, #HALF-WIDTH#,  
225X, #POSITION#)
NTOT=NTOT+3*NSING
DO 180 I=NL,NTOT,3
NSUB=I+2
AREA = P02*B(I+1) * B(I)
PRINT 299, (B(J), B(J), J=I,NSUB), AREA
PUNCH 200,B(I),B(I+1),B(I+2)
A(KK) = B(I) 
$ A(KK+1) = B(I+1)  \$  A(KK+2) = B(I+2) 
KK = KK+3

180 CONTINUE
190 CONTINUE
195 KK=KK+1
IF (NPLT.EQ.0) GO TO 1
NPLT = NPLT + 1
CALL NLLSOPT (Y,A,KK,NPLT,3,NSUB, vmax, vmin, res, title, CG, VELC,  
1NPLT)
GO TO 1

901 CONTINUE
IF (MOD(NPLT,4).NE.0) CALL PLOTEND
END FILE 10
SUBROUTINE CALIB(B,NPAIR,CG,VELC)
DIMENSION B(45), V(3)

C THIS SUBROUTINE CALCULATES THE CALIBRATION CONSTANTS FOR AN IRON FOIL SPECTRUM.
DATA V/1.6779,6.167,10.657/
VELC = CG = HTTOT = 0.
J=2
DO 10 I=1,NPAIR
SPLIT = ABS(B(J+3) - B(J+2))
VELC = VELC + B(J) * V(NPAIR + 1 - I) / SPLIT
CG = CG + B(J) * (S(J+2) + SPLIT/2) /
HTTOT = HTTOT + B(J)
10 J=J+4
VELC = VELC/HTTOT
CG = CG/HTTOT
RETURN
END
SUBROUTINE MODEL(F,Y,X,RRR,I,JP)
COMMON/BLK1/P(45),PARTIAL(45),RE,N,H,NPARAMS
COMMON/DATA5/NPAIRS,NSING
DIMENSION X(1),Y(1),RRR(1)
PARTIAL(1)=1.0
710 F=P(1)
NUM=5*NPAIRS+1
IF (NUM.LE.2) GO TO 705
DO 704 K = 2,NUM,5
HT = P(K)
GAM = P(K+1)
P1 = P(K+2)
P2 = P(K+3)
R = P(K+4)
HT2 = HT/R
GAM2 = GAM*R
RGAM = 2./GAM
RGAM2 = 2./GAM2
RGMASQ = RGAM*RGMAM
RGMASQ = RGMAM*RGMAM
DIS1 = X(I) - P1
DIS2 = X(I) - P2
DIS1Q = DIS1**2
DIS2Q = DIS2**2
DENOM1 = DIS1Q*RGAMASQ + 1.
DENOM2 = DIS2Q*RGAMASQ + 1.
DISQ = DIS1Q*DENOM1
DENOM2 = DIS2Q*DENOM2
PARTIAL(K) = -(1./DENOM1 + 1.)/(R*DENOM2)
PARTIAL(K+1) = -(HT*DIS1Q*RGAMASQ/DISQ + 1.)
PARTIAL(K+2) = -2.*HT*DIS1Q*RGAMASQ/DISQ
PARTIAL(K+3) = -2.*HT2*DIS2Q*RGAMASQ/DISQ
PARTIAL(K+4) = (HT/(R*DENOM2))*(1. - 2.*DIS2Q*RGAMASQ/DENOM2)
F = F - HT/DENOM1 - HT2/DENOM2
705 NUM=NUM+1
IF(NUM.GT.NPARAMS) GO TO 707
DO 720 K2=NUM,NPARAMS+3
K3=K2+1
K4=K2+2
Z=(2.0/P(K3))**2
W1=X(I)-P(K4)
G1=W1**2
U1=(G1+1.0)
FN1=U1**2
D1=P(K2)/FN1
PARTIAL(K2)=(-1.0/U1)
PARTIAL(K3)=((-6.0*DI*G1)/(P(K3)**3))
PARTIAL(K4)=(-2.0*DI*W1**2)
F=F+(F*(PARTIAL(K2))
707 CONTINUE
704 CONTINUE
705 CONTINUE
720 CONTINUE
END
SUBROUTINE NLLSQ(Y,X,BB,RES,NARRAY,ARRAY,IBB,FMT)
C
NONLINEAR LEAST SQUARES FITTING ALGORITHM BY D W MARQUARD
C
ORIGINAL PROGRAM REWRITTEN BY W A BURNETTE BTL JULY 1967
C
NARRAY CONTAINS PROGRAM PARAMETERS ARRAY CONTAINS STATISTICAL
C
CONSTANTS SET ARRAY EQUAL TO 0 FOR STANDARD SET OF CONSTANTS
C
MAXIMUM NUMBER OF PARAMETERS IS 45 THIS MAY BE CHANGED BY ALTERING
C
DIMENSION STATEMENTS AND MATRIX STORING STATEMENTS
C
COMMON/BK1/B(45),P(45),RE,N,M,K
C
COMMON/BK2/A(90,45),SA(45),K2,IK,NPMAX
C
COMMON/BK3/BS(45),DB(45),G(45),K3
C
COMMON/BK4/AL,DELTA,E,FF,GAMCR,T,TAU,ZETA,PHI,SE,PHICR
C
COMMON/BK5/IB(45),IP
C
DIMENSION Y(1),X(1,1),RES(1)
C
DIMENSION BB(45),IBB(45)
C
DIMENSION FMT(45)
C
DIMENSION NARRAY(8),ARRAY(9)
C
DIMENSION CONST(8),SCONST(8)
C
EQUIVALENCE(CONST,AL)
C
DATA (SCONST=0.1,1.3E-5,5.0E-5,4.0,45.0,2.0,0.001,1.0E-31)
C
NPMAX=45
C
N=NARRAY(1)
C
M=NARRAY(2)
C
K=NARRAY(3)
C
K2=K
C
K3=K
C
IP=NARRAY(4)
C
INTP=NARRAY(5)
C
IFF=NARRAY(6)
C
IK=NARRAY(7)
C
IF(NARRAY(8).EQ.-1) NARRAY(8)=KITER
C
KITER=NARRAY(8)
C
WHICH OF THE CONSTANTS HAVE BEEN DETERMINED BY USER
C
DO 5 J=1,8
C
IF(NARRAY(J).LE.0) GO TO 4
C
CONST(J)=NARRAY(J)
C
GO TO 5
C
4
C
CONTINUE
C
IF(KITER.LE.0) KITER=30
C
IF(IK.LE.0) IK=6
C
26 IF(IFF.EQ.-1) GO TO 100
C
WRITE(IK,2090)
C
WRITE(IK,FMT)
C
WRITE(IK,2001) N,K,M,OELTA,E,FF,GAMCR,T,TAU,ZETA,AL
C
100
C
DO 120 J=1,K
C
BS(J)=BB(J)
C
B(J)=BE(J)
C
120 CONTINUE
C
DO 121 J=1,IP
C
121 IB(J)=IBB(J)
C
CALL SUMSQ(PHI,Y,X,RES)
C
LJ=0
C
130 IF(LJ.GE.KITER) GO TO 404
C
LJ=LJ+1
C
BEGIN LJTH ITERATION
C
CALL NEWA(Y,X,RES)
C
131 IF(ALT.1E-07) GO TO 131
AL = AL/10.

131 CALL SCAL
PHI0 = PHI

C STORE MATRIX
DO 132 I=1,K
II=I+NPMAX
DO 132 J=1,K
132 A(II,J) = A(I,J)

CALL SOLVE
135 DO 140 J=1,K
140 B(J) = BS(J)+DB(J)

C COMPUTE GAMMA
150 DD = 0.
DG = 0.
GG = 0.
DO 152 J=1,K
IF (SA(J) .EQ. 0.) GO TO 152
GG = GG + G(J)/SA(J)
DO = DD + DB(J)*DB(J)*SA(J)
152 X = SQRT(DO)
IF (DG*DG+GG.GT.0.) GO TO 160

GAMMA = 0.
GO TO 170

160 GAMMA = DG/SQRT(DO*GG)

IF (GAMMA .GE. 1.) GO TO 170

WS = SQRT(1.-GAMMA*GAMMA)
GAMMA = 57.2957795*ATAN2(WS,GAMMA)

170 CALL SUMSQ(PHI,Y,X,RES)
171 IF (PHI.LE.PHI0) GO TO 175
175 DO 176 J=1,K
176 BS(J) = B(J)

IF (GAMMA.LT.90.) GO TO 190

C GAMMA LAMBDA TEST
178 IF (AL1.190,403,433
180 AL = AL*10.

CALL SOLVE
GO TO 135

C EPSILON TEST
190 CALL ETEST(L)
GO TO (401,200),L

C BEGIN INTERMEDIATE OUTPUT ROUTINE
210 IF (INTP.EQ.0) GO TO 130

WRITE (IK,2000)
WRITE (IK,2002) L, PHI0, AL, (B(J), J=1,K)
WRITE (IK,2003) GAMMA, (CB(J), J=1,K)
IF (INTP.EQ.1) GO TO 130

CALL NEWA(Y,Y,X,RES)

C STORE MATRIX
DO 205 I=1,K
II=I+NPMAX
DO 205 J=1,K
205 A(II,J) = A(I,J)

CALL GJR(MS)
GO TO (207,130), MS
207 IF(IHF.EQ.2) GO TO 210
    WRITE(IK,2004)
    CALL PRINT1
210 CALL SCAL
    WRITE(IK,2066)
    CALL PRINT2
C GET MATRIX FROM STORAGE
   DO 220 I=1,K
      II=I+NPMAX
   DO 220 J=1,K
220 A(I,J)=A(II,J)
   IF(LJ.GE.KITER) GO TO 404
   LJ=LJ+1
   GO TO 1311
300 DO 320 J=1,K
   DB(J)=DB(J)/2.
320 B(J)=BS(J)+DB(J)
C GAMMA EPSILON TEST
   CALL ETEST(L)
   GO TO (402,321),L
321 CALL SUMSQ(PHI,Y,X,RES)
   IF(PHIOLD.LT.PHI) GO TO 300
   DO 330 J=1,K
330 BS(J)=B(J)
   GO TO 200
C BEGIN FINAL PRINTOUT ROUTINE
401 IF(IFP.EQ.(-1)) GO TO 600
   WRITE(IK,FMT)
402 IF(IFP.EQ.(-1)) GO TO 6025
   WRITE(IK,FMT)
403 IF(IFP.EQ.(-1)) GO TO 603
   WRITE(IK,FMT)
404 WRITE(IK,2013)
   NARRAY(8)=-1
   IF(IFP.EQ.(-1)) GO TO 600
   WRITE(IK,FMT)
405 DO 406 J=1,K
406 BS(J)=B(J)
   WRITE(IK,2062) J,PHI,AL,(B(J), J=1,K)
   WRITE(IK,2003) GAMMA,XL9(08(J), J=1,K)
   CALL NEWA(Y,X,RES)
IF(IFP.LE.1)GO TO 430
DO 410 I=1,K
II=I*NPMAX
DO 410 J=1,K
410 A(II,J)=A(I,J)
WRITE(IK,2022)
CALL PRINT1
CALL SCAL
WRITE(IK,2023)
CALL PRINT2
C GET MATRIX FROM STORAGE
DO 420 I=1,K
II=I*NPMAX
DO 420 J=1,K
420 A(I,J)=A(II,J)
430 CALL GJR(MS)
GO TO (440,435),MS
435 WRITE(IK,2060)
GO TO 455
440 IF(IFP.EQ.0)GO TO 450
WRITE(IK,2024)
CALL PRINT1
450 CALL SCAL
WRITE(IK,2025)
CALL PRINT2
455 IF(IFP.EQ.0)GO TO 590
GO TO 461
WRITE(IK,2030)
DO 460 I=1,N
C RESIDUAL ARRAY OPTION SATISFIED HERE
J=4
CALL MODEL(F,Y,X,RES,I,J)
460 WRITE(IK,2031)I,Y(I),F,RES
461 CONTINUE
C ONE PARAMETER SUPPORT PLANE COMPUTATIONS
FNKW=N-K+IP
IF(FNWK.LE.0)GO TO 589
FKW=K-IP
SE=SORT(PHI/FNKW)
WRITE(IK,2040)
DO 470 I=1,K
C CHECK FOR OMITTED PARAMETERS
IF(IP.EQ.0)GO TO 464
DO 462 J=1,IP
IF(I.EQ.IB(J))GO TO 469
464 STE=SA(I)*SE
HJTD=SORT(FF*FKW1mSTE
OPL=BS(I)-HJTD
OPL=BS(I)-STE
SPL=BS(I)+HJTD
SPL=BS(I)+STE
WRITE(IK,2041)I,STE,OPL,OPU,SPL,SPU
GO TO 470
469 WRITE(IK,2042)
470 CONTINUE
IF (IFF.EQ.1) GO TO 602
NONLINEAR CONFIDENCE REGION CALCULATIONS
WS=FKW/FNKW
PHIC=[FH=[X+WS*FF]
WRITE(IK,2049)PHICR
CALL CONFRG(Y,X,RES)
IF(IFR.GE.0)WRITE(IK,2090)
RETURN
598 WRITE(IK,2060)
599 IF(IFP.EQ.0) GO TO 602
599 IF(IFP.GE.0)WRITE(IK,2090)
RETURN
C RETURNING PARAMETERS WITH NO OUTPUT
600 DO 601 J=1,K
601 B(J)=B(J)
C RESIDUAL ARRAY OPTION WITH NO OUTPUT
602 J=4
CALL MODEL(F,Y,X,RES,1,J)
GO TO (599,599,599,604),J
604 DO 605 I=2,N
605 CALL MODEL(F,Y,X,RES,1,J)
IF(IFP.GE.0)WRITE(IK,2090)
RETURN
2000 FORMAT(100H0XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX/1H0)
2001 FORMAT(1H0NO OF DATA POINTS IS,I4,22H NO OF PARAMETERS IS,I3,3X
1309HC NO OF DEPENDENT VARIABLES IS,I3/7MODEL=,E15.8,5H E=,E15.
26,6H FF=,E15.8,9H GAMCR=,E15.8/5H T=,E15.8,7H TAU=,E15.8,
38H ZETA=,E15.8,6H AL=,E15.8 )
2002 FORMAT(I1X/19H0NO OF ITERATIONS =I3/6M0PHI =,E15.8,4X,8H0LAMDA =,
1E15.8/110PARAMETERS/(1X,7E17.8/))
2003 FORMAT(8H0GAMMA =,E15.8,4X,14HLENGTH OF DB =,E15.8/21M0DB CORRECTI
1ON VECTOR/(1X,7E17.8/))
2004 RETURN(I1X/12M0PTP INVERSE)
2006 FORMAT(I1X/25H0CORRELATION COEFFICIENTS)
2010 FORMAT(23H0CONVERGENCE BY EPSILON TEST)
2011 FORMAT(5H0CONVERGENCE BY GAMMA EPSILON TEST)
2012 FORMAT(3H0CONVERGENCE BY GAMMA LAMBDA TEST)
2013 FORMAT(18H0FORCE OFF)
2122 FORMAT(I1X/11M0PTP MATRIX)
2123 FORMAT(I1X/29M0PTP CORRELATION COEFFICIENTS)
2124 FORMAT(I1X/12M0PTP INVERSE)
2125 FORMAT(I1X/35M0PARAMETER CORRELATION COEFFICIENTS)
2130 FORMAT(I1X/19,6X,11H OBSERVED,11X,9HPREDICTED,11X,8HRESIDUAL/1X)
2131 FORMAT(I1X,13,3X,2I15,8,4X),E15.8)
2140 FORMAT(I1X/130,12X,5H STD,18X,15HONE - PARAMETER,22X,13HSUPPORT PLA
1NE/27,4HPARA,7X,15HERR,13X,5LOWER,13X,5UPPER,13X,5MLOWER,13X,5M
UPPER)
2141 FORMAT(I1X,13,5E15.8)
2142 FORMAT(I1X,13,5X,23H0PARAMETER HELO CONSTANT)
2149 FORMAT(I1X/29M0 NONLINEAR CONFIDENCE LIMITS/15M0PHI CRITICAL =E15.8
1/6M0 PARA,6X,8H LOWER 8,8X,10H LOWER PHI,10X,8H UPPER 8,8X,10H UPP
ER PHI)
2160 FORMAT(I57H0OUTPUT IS ABBREVIATED DUE TO MATHEMATICAL CONSIDERATION
15)
2190 FORMAT(I1M)
2192 FORMAT(50H0CORRECTION VECTOR FOR LAST ITERATION WAS NOT USED)
END
SUBROUTINE NEWA(Y,X,RES)
C
NEWA - CALCULATES PTP MATRIX, A, AND GRADIENT VECTOR, G.
C
DIMENSION Y(1),X(1,1),RES(1)
COMMON/BLK1/BL(45),P(45),RE,N,M,K
COMMON/BLK2/A(90,45),SA(45),K2,IK,NPMAX
COMMON/BLK3/13S(45),D3(45),G(45),K3
COMMON/BLK4/AL,DELTA,E,FF,GAMCR,T,TAU,2ETA,PHI,SE,PHICR
COMMON/BLK5/IB(45),IP
DO 1 J=1,K
G(J)=0.
P(J)=0.
1 DO 1 I=1,K
A(I,J)=0.
DO 50 II=1,N
C
LOOK FOR PARTIALS
J=2
CALL MODEL(F,Y,X,RES,II,J)
RD=RE
10 DO 30 JJ=1,K
C
CHECK FOR OMITTED PARAMETERS
IF(IP.GT.0)GO TO 25
GO TO(20,30,20),J
C
COMPUTE PARTIALS IF NECESSARY
20 AB=B(JJ)
BOEL=AE*DELTA
IF(BOEL.EQ.0.)BOEL=DELTA
B(JJ)=AB+BOEL
J=1
CALL MODEL(FDEL,Y,X,RES,II,J)
RE=RD
P(JJ)=(FDEL-F)/BOEL
B(JJ)=AB
GO TO 30
25 DO 26 I=1,IP
IF(JJ.EQ.IB(I)) GO TO 29
26 CONTINUE
GO TO 10
29 P(JJ)=0.
C
USING PARTIALS AT ITH DATA POINT
30 G(JJ)=G(JJ)+RE*P(JJ)
40 A(I,J)=A(I,J)+P(I)*P(J)
50 CONTINUE
GO TO 55
55 A(I,J)=A(I,J)
C
A(I,I)=1.0 FOR OMITTED PARAMETER I
IF(IF.EQ.0.)RETURN
GO 60 I=1,IP
GO 60 J=1,K
60 IF(JJ.EQ.IB(I))A(J,J)=1.
RETURN
END
SUBROUTINE GJR(MSING)
C  INVERTS A MATRIX IN A(I,J), I=1,45, J=1,45
C  GAUSS-JORDAN-RUTISHAUSER MATRIX INVERSION WITH DOUBLE PIVOTING
COMMON/A/LK2A(45),SA(45),K2,IK,NMAX
COMMON/B/LK4/AL,DELTA,E,FF,GAMCR,T,TAU,ZETA,PHI,SE,PHICR
DIMENSION P(+5),Q(+5),R(45),C(45)
INTEGER P(0),Q,
EPS=ZETA
N=K2
MSING=1
DO 10 K=1,N
C  DETERMINATION OF PIVOT ELEMENT
PIVOT=0.
DO 20 I=K,N
DO 20 J=K04
IF(ABS(A(I,J))-A3S(PIVOT))20.20,30
30 PIVOT=A(I,J)
P(K)=I
Q(K)=J
20 CONTINUE
IF(ABS(PIVOT)-EPS)40.40,50
C  EXCHANGE OF PIVOTAL ROW WITH KTH ROW
50 IF (P(K).E0.K) GO TO 80
DO 70 J=1,(L=P(K)
Z =A (L,J)
A(L,J)=A(K,J)
70 A(K,J)=Z
C  EXCHANGE OF COLUMN
80 IF(C(K).E0.K) GO TO 90
DO 100 I=1,N
L=Q(K)
Z=A(I,L)
A(I,L)=A(I,K)
100 A(I,K)=Z
90 CONTINUE
C  JORDAN STEP
DO 110 J=1,N
IF(J.E0.K) GO TO 120
B(J)=-A(K,J)/PIVOT
C(J)=A(J,K)
GO TO 140
120 B(J)=1./PIVOT
C(J)=1.
140 A(K,J)=0.
110 A(J*K)=0.
DO 10 J=1,N
DO 10 I=1,N
10 A(I,J)=A(I,J)+C(I)*B(J)
C  REORDERING THE MATRIX
DO 155 M=1,N
K=N-M+1
IF (F(K),E0.K) GO TO 170
DO 180 I=1,N
L=P(K)
Z=A(I,L)
A(I,L)=A(I,K)
SUBROUTINE SUMSQ(Phi,Y,X,RES)
COMPUTES SUM OF SQUARES
DIMENSION Y(1), X(1,1), RES(1)
COMMON/BLK1/8(45),P(45),RE,N,M,K
Phi=0.
DO 10 I=1,N
CALL MODEL(F,Y,X,RES,I,1)
10 Phi=Phi+RE*RE
RETURN
END

SUBROUTINE SCAL
SCALES ACCORDING TO DIAGONAL ELEMENTS
COMMON/BLK2/A(90,45),SA(45),K2,IK,NPMAX
K=K2
DO 20 I=1,K
IF(A(I,I).GT.0.) GO TO 15
SA(I)=0.
GO TO 20
15 SA(I)=SQRT(A(I,I))
20 CONTINUE
DO 50 I=1,K
DO 40 J=1,K
WS=SA(I)*SA(J)
IF(WS.GT.0.) GO TO 30
A(I,J)=0.
GO TO 40
30 A(I,J)=A(I,J)/WS
40 A(J,I)=A(I,J)
50 A(I,I)=1.0
RETURN
END
SUBROUTINE SOLVE
C SOLVES (PTP)(08)=(G) WHERE PTP IS STORED IN A(I+20,J)
C SOLVES A SET OF LINEAR EQUATIONS IN DB DETERMINED BY MATRIX
C A AND VECTOR G. USES SUBROUTINE GJR TO INVERT MATRIX
COMMON/BLK2/A(90,45),SA(45),K2,NMAX
COMMON/BLK3/BS(45),G(45),K3
COMMON/BLK4/AL,DELTA,E,FF,GAMCR,T,TAU,ZETA,PHI,SE,PHICR
K=K2
L=1
C GET MATRIX FROM STORAGE
1 DO 10 I=1,K
II=I+NMAX
10 A(I,J)=A(II,J)
9 A(I,J)=A(I,J)+AL
20 CALL GJR(MS)
GO TO (25,110),MS
25 DO 40 I=1,K
OB(I)=0.
30 IF(SA(I).LE.0.)GO TO 30
30 OB(I)=A(I,J)*G(J)/SA(J)+OB(I)
CONTINUE
DB(I)=OB(I)/SA(I)
40 CONTINUE
RETURN
100 AL=AL+10.
L=L+1
IF(L.GE.6)STOP
GO TO 1
END

SUBROUTINE ETEST(ML)
COMMON/BLK1/B(45),P(45),RE,N,M,K
COMMON/BLK3/BS(45),G(45),K3
COMMON/BLK4/AL,DELTA,E,FF,GAMCR,T,TAU,ZETA,PHI,SE,PHICR
EPS=E
ML=1
DO 20 I=1,K
W=ABS(DB(I))/TAU+ABS(B(I))
20 IF (W.GE.EPS) GO TO 30
CONTINUE
GO TO 40
30 ML=2
40 RETURN
END
SUBROUTINE PRINT1
PRINTS A K BY K SINGLE PRECISION MATRIX
COMMON/BLK2/A(90,45),SA(45),K2,IK,NPMAX
K=K2
L=1
JJ=7*L
LL=JJ-6
IF(K,LT,LL)GO TO 30
IF(K,LT,JJ)GO TO 20
WRITE(IK,105)LL,JJ
DO 15 I=1,K
15 WRITE(IK,106)(A(I,J),J=LL,JJ)
L=L+1
GO TO 5
20 WRITE(IK,105)LL,K
DO 25 I=1,K
25 WRITE(IK,106)(A(I,J),J=LL,K)
30 RETURN
105 FORMAT(1X/8H000COLUMNSTI4OHTHROUGH,I4)
106 FORMAT(1X,7E17.8)
END

SUBROUTINE PRINT2
PRINTS A K BY K CORRELATION COEFFICIENT MATRIX
COMMON/BLK2/A(90,45),SA(45),K2,IK,NPMAX
L=1
K=K2
JJ=13*L
LL=JJ-12
IF(K,LT,LL)GO TO 30
IF(K,LT,JJ)GO TO 20
WRITE(IK,105)LL,JJ
DO 15 I=1,K
15 WRITE(IK,107)(A(I,J),J=LL,JJ)
L=L+1
GO TO 5
20 WRITE(IK,105)LL,K
DO 25 I=1,K
25 WRITE(IK,107)(A(I,J),J=LL,K)
30 RETURN
105 FORMAT(1X/8H000COLUMNSTI4OHTHROUGH,I4)
107 FORMAT(1X,13F9.4)
END
SUBROUTINE CONFRG(Y,X,RES)

CONFRG - NON LINEAR CONFIDENCE REGION CALCULATIONS

COMM/N/BLK1/9(N51),P(45),RE,N,M,K
COMM/N/BLK2/A(90,45),SA(45),K2,IK,PMAX
COMM/N/BLK3/BS(45),I&(45),G(45),K3
COMM/N/BLK4/45,DELTA,E,FF,GAMCR,T,TAU,ZETA,PHI,SE,PHICR
COMM/N/BLK5/IV(45),IP
DO 583 J=1,K
NOLO=0
C
CHECK FOR OMITTED PARAMETERS
IF(IP.EQ.0) GO TO 509
DO 504 I=1,IP
IF(J.EQ.IB(I))GO TO 506
504 CONTINUE
GO TO 509
506 WRITE(IK,2042)J
GO TO 580
509 D=0.
510 D=D+S
DJ=SE*SA(J)
B(J)=BS(J)+D*DJ
CALL SUMSQ(PH,Y,X,RES)
IF(PH.LT.PHICR)GO TO 530
520 D=0/2.
IF(ABS(D).LT.0.01)GO TO 570
B(J)=BS(J)+D*DJ
CALL SUMSQ(PH,Y,X,RES)
IF(PH-PHICR).LT.540,540,520
530 D=0*DS
IF(ABS(D).LT.5.0)GO TO 570
B(J)=BS(J)+D*DJ
CALL SUMSQ(PH,Y,X,RES)
IF(PH-PHICR).LT.570,570,530
540 Q=1.-Q
XK1=PHI/D+PH/D+PPH/(Q*D)
XK2=PHI*(1.+Q)/D+PHD/Q+PPH/(D*Q)
XK3=PHI-PHICR
BC=*(XK2**2 -4.*XK1*XK3)/(2.*XK1)
IF(ODS.GT.0.) GO TO 550
B(J)=BS(J)-BC*DJ
BL=BJ
CALL SUMSQ(PH,Y,X,RES)
548 D=1.
GO TO 510
550 B(J)=BS(J)+D*DJ
BL=BJ
CALL SUMSQ(PH,Y,X,RES)
GO TO 576
570 IF(ODS.GT.0.) GO TO 571
NOLO=1
GO TO 549
571 IF(NOLO.NE.0) GO TO 575
C
OMITTING UPPER LIMITS
WRITE(IK,2055)J,BL,PL
GO TO 580
C
OMITTING BOTH
575 WRITE(IK,2056)J
SUBROUTINE BOX(X,Y)
DIMENSION CUTOUT(2)
DATA CUTOUT/UNCUT ALONG SOLID LINE/
CALL VECTORS
XX = X - 1.5
YY = Y - 1.
CALL SCALE (1.,1.,XX,YY,0.,0.)
CALL PLOT(0.,0.,0.,0.)
CALL PLOT (1.,0.,1.,0.)
CALL PLOT (1.,8.5,1.,0.)
CALL PLOT (0.,8.5,1.,0.)
CALL PLOT (0.,0.,1.,0.)
CALL POINTS
CALL PLOT (1.25,8.2,1,28)
CALL PLOT (5.56,8.2,1,28)
CALL PLOT (9.75,8.2,1,28)
CALL SYMBOL (4.3,8.55,0.,12.,2C,CUTOUT)
CALL VECTORS
RETURN
END
SUBROUTINE NLLSOPT (Y,3,OPARMS,NPLT,NZERO1,NTOT,YMAX,YMIN,RES,
1ITLE,CG,VELC,ITYPE)
DIMENSION Y(512),RES(512),B(45)
DIMENSION TITLE(10),ARRAY(10)
CALL FLOTLUN(10)
NTYPE = 0
IF(ITYPE.LT.0)NTYPE = 3
CALL FLOTYPES(NTYPE)
JCOUNT = MOD(NPLT - 1,4)
XOFF = 2.
YOFF = 2.*10.*JCOUNT
CALL SIZE(26.,YOFF+8.)

DRAW BOX AROUND THE DATA AND MODEL PLOT

CALL BOX(XOFF,YOFF)

AUTOSCALE Y IF YMAX EQUALS ZERO

IF (YMAX.NE.0.) GO TO 2
YMIN = YMAX = Y(NZERO1)
DO 1 = NZERO1,NTOT
IF (Y(I).LT.YMIN) YMIN = Y(I)
1 CONTINUE
YMAX = YMAX = YMAX - Y(YMIN)
YDIF = YMAX - YMIN
YDIF = YDIF/2.0
XSCAL = 8.5455/XDIF
YSCAL = 6.5636/YDIF
CALL VECTORS
CALL SCALE (XSCAL,YSCAL,XOFF,YOFF,XMIN,YMIN)

DRAW X AXIS FOR DATA PLOT

ENCODE (4,310,ARRAY) XMIN
310 FORMAT(F4.0)
CALL SYMBOL (XMIN=XXDIS,YMIN=XYDIS,0.,16.4,ARRAY)
CALL PLOT (XMIN,YMIN,0.0)
CALL PLOT (XMIN,YMIN,1.6)
XP = XP = NZERO1/10
320 IF (XP.GE.XMAX) GO TO 330
CALL PLOT (XP,YMIN,1.8)
GO TO 320
330 CALL PLOT (XMAX,YMIN,1.8)
310 ENCODE (4,310,ARRAY) XMAX
CALL SYMBOL (XMAX=XXDIS,YMIN=XYDIS,0.,16.4,ARRAY)
CALL PLOT (XMIN,YMIN,0.0)
DRAW AND LABEL Y AXIS FOR DATA PLOT

YP=YP=YPMIN
IPP=YPMIN+5
YLMK=YP+1
YHMK=IPP=YMAX
YP=YP+5

IF (YP,ZE.IPP) GO TO 350
340 CALL PLOT (XMIN,YP,1,5)
350 YP=YP+5
CALL PLOT (XMIN,YP,1,6)
YP=YP+5
IF (YP,ZE.YLMK) GO TO 340
IF (YP,ZE.YMAX) GO TO 360
CALL PLOT (XMIN,YP,1,5)
360 CALL PLOT (XMIN,YMAX,1,0)
ENCODE (4,310,ARRAY) YLMK
CALL SYMBOL (XMIN,XYDIS,YLMK,YDIS,0.0,16,4,ARRAY)
ENCODE (4,310,ARRAY) YHMK
CALL SYMBOL (XMIN,XYDIS,YHMK,YDIS,0.0,16,4,ARRAY)
ENCODE (72,20,ARRAY) (TITLE(I),I=1,9)
CALL SYMBOL (XMIN,YMAX,0.0,12,72,ARRAY)

PLOT DATA

CALL POINTS
DO 370 I=NZERO1,NTOT
FI=I
370 CALL PLOT (FI,Y(I),1,1)

PLOT MODEL AS Y(I) - RES(I)

CALL VECTORS
CALL PLOT (XMIN,Y(NZERO1)-RES(NZERO1),0,0)
DO 450 I=NZERO1,NTOT
FI=I
450 CALL PLOT (FI,Y(I)-RES(I),1,0)

DRAW VERTICAL LINE TO INDICATE POSITION AND HEIGHT OF EACH PEAK

DO 460 I=2,NPARMS,3
CALL PLOT (B(I+2),B(1),0,0)
CALL PLOT (B(I+2),B(1)-B(I),1,5)
HTZ = B(I)+B(I)/2.
GAM2 = B(I+1)/2.
CALL PLOT(B(I+2)-GAM2,HTZ,0,0)
CALL PLOT(B(I+2)-GAM2,HTZ,1,7)
460 CALL PLOT(B(I+2)+GAM2,HTZ,1,7)

IF (CG,LE.0.0) GO TO 600

WRITE CENTER OF GRAVITY AND CALIBRATION CONSTANT ON PLOT IF
CG IS NON-ZERO.

ENCODE (65,700,ARRAY) VEIL,CG
This code generates the velocity axis on the data plot if CG is non-zero. For this section, the following parameters are important:

- VELMIN = minimum in velocity corresponding to XMIN.
- VELMAX = maximum in velocity corresponding to XMAX.
- VAX = offset of velocity axis above channel axis (.5 inches above).
- VLMK = low value on vel axis to be labeled.
- VMMX = high value on vel axis to be labeled.

Set up initial parameters required.

- VELMIN = (XMIN-CG)*VELC
- VELMAX = (XMAX-CG)*VELC
- VEL1 = 1./VELC
- VLMK = IVL = VELMIN
- DEL = VLMK - VELMIN
- VAX = .5/YSCAL + YMIN
- VMHK = IVH = VELMAX

Draw velocity axis.

- CALL PLOT(XMIN,VAX,0,0)
- VPOS = XMIN + DEL/VELC
- CALL PLOT(VPOS,VAX,1,8)
- VPOS = VPOS + VEL1
- If (VPOS.LE.XMAX) GO TO 800
- CALL PLOT(XMAX,VAX,1,0)

Label velocity axis at VLMK, O. and VMHK.

- VPOS = CG - .04/XSCAL
- CALL SYMBOL(VPOS,VAX-YXD1S,0...16,1,1H)
- VPOS = CG + VMHK * VEL1
- ENCODE (3,820,ARRAY) IVL

Draw vertical line at VEL = 0.

- CALL PLOT(CG,100,0,0)
- CALL PLOT(CG,VAX,1,0)

Continue.

Print cut Lorentz info on plot.

- ENCODE (18,10G,ARRAY) B(1)

Format (2X,SKG = #:F10.5)
- CALL SYMBOL(XMIN,YMAX=.4/YSCAL,0...12,18,ARRAY)
- K=1
- L = 2
- DO 120 I=2,NPARMS,3
CHANGE GAMMA AND POS TO VELOCITY UNITS IF CALIBRATION INFO AVAILABLE

IF (VELC.EQ.0.) GO TO 1100
B(I+1) = B(I+1) * VELC
B(I+2) = (B(I+2) - CG) * VELC

ENCODE (70, 110, ARRAY) K, B(I), K, B(I+1), K, B(I+2)

K = K + 1
L = L + 1
IF (L.EQ.8) L = 25
CALL SYMBOL (XMIN, YMAX - (L*2/YSCAL), 0..12, 70, ARRAY)

CONTINUE

XOFF = 15.

DRAW BOX AROUND THE RESIDUAL PLOT
CALL BCX(XOFF, YOFF)

START RESIDUAL PLOT WORK BY AUTOSCALING RES

RESMIN = RESMAX = 0.
DO 500 I = NZERO1, NNTOT
   IF (RES(I).GT. RESMAX) RESMAX = RES(I)
   IF (RES(I).LT. RESMIN) RESMIN = RES(I)
   ROIF = 0.1
   RSCAL = 6.5636/(RDIF*2.)
   CALL SCALE (XSCAL, RSCAL, XOFF, YOFF, XMIN, -ROIF)
   RDDIS = .24/RSCAL
   CALL PLOT (XMIN, 0.)
   XP = XP + 10.
   IF (XP.GE. XMAX) GO TO 630
   CALL PLOT (XP, 0., 1.)
   GO TO 620

CALL PLOT (XMAX, 0., 1.)
ENCOD (4, 610, ARRAY) XMAX

FORMAT (F4.0)
CALL SYMBOL (XMIN-XDIS, -RXDIS, 0..16, 4, ARRAY)
CALL PLOT (XMIN, 0., 0., 0.)
CALL PLOT (XMIN, 0., 1., 0.)
XP = XMIN / NZERO1/10

IF (XP.GE. XMAX) GO TO 630
CALL PLOT (XP, 0., 1., 0.)
GO TO 620

CALL PLOT (XMAX, 0., 1., 0.)
ENCOD (4, 610, ARRAY) XMAX
CALL SYMBOL (XMAX-XDIS, -RXDIS, 0..16, 4, ARRAY)

DRAW Y AXIS FOR RESIDUAL PLOT

CALL PLOT (XMIN, 0..0, 0.)
R=0.

CALL PLOT (XMIN, R, 1., 0.)
R=R+1
IF (R.LT. ROIF) GO TO 510
CALL PLOT (XMIN, ROIF, 1., 0.)
CALL PLOT (XMIN, 0., 0., 0)
  R = -.1
530 CALL PLOT (XMIN, R+.1, 0)
  R = R -.1
IF (R .GT. -ROIF) GO TO 530
CALL PLOT (XMIN, -ROIF+.1, 0)
C  C  C
C  LABEL Y AXIS
C
RLABEL = R + .1
R = RLABEL
525 ENCODE (4, 520, ARRAY) RLABEL
520 FORMAT (F4.1)
CALL SYMBOL (XMIN-XDIS, RLABEL-RDIS+.0...16, 4, ARRAY)
RLABEL = RLABEL - R
IF (RLABEL .LE. ROIF) GO TO 525
C  C  C
WRITE TITLE ON RES PLOT
C
ENCODE (72, 23, ARRAY) (TITLE(I), I = 1, 9)
CALL SYMBOL (XMIN, RDIS+.0...12, 72, ARRAY)
NPEAKS = NPARMS/3
ENCOD(9, 900, ARRAY) NPEAKS
900 FORMAT (I2 FOR *PEAK MODEL*)
CALL SYMBOL (XMIN, RDIS-.2/RSCAL+.0...12, 19, ARRAY)
20 FORMAT (16A8)
C  C  C
PLOT RESIDUALS
C
CALL PLOT (XMIN, RES(NZERO1), 0, 0)
DO 670 I = NZERO1, NTOT
  FI = I
670 CALL PLOT (FI, RES(I), 1, 0)
IF (JCOUNT.EQ.3) CALL PLOTEND
RETURN
END