

AN ABSTRACT OF THE THESIS OF

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CYTOCHROME P-450

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Abstract approved: _____
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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, ΔE_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.

Magnetic Properties of an Analog Compound
for Cytochrome P-450

by

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TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION.	1
II. EXPERIMENTAL.	8
A. Materials	8
B. Mossbauer Methodology	9
C. Magnetic Susceptibility Apparatus	10
D. Electron Paramagnetic Resonance Apparatus	12
III. THEORY.	14
A. Introduction.	14
B. Ground State Interactions	19
1) Low Spin Iron (III).	19
2) High Spin Iron (III)	24
C. Hyperfine Interactions.	26
D. Relaxation Theory	35
E. Effect of Small External Magnetic Fields.	42
IV. CALCULATIONS.	44
V. EXPERIMENTAL RESULTS.	58
A. Mossbauer Data.	58
B. Magnetic Susceptibility Data.	58
C. Electron Paramagnetic Resonance Data.	65
VI. DATA ANALYSIS	67
A. Mossbauer Spectra	67
B. EPR and Susceptibility Measurements	75
C. Correlation of EPR and Mossbauer Data	76
VII. CONCLUSIONS	86
BIBLIOGRAPHY.	90
APPENDIX I. Programs MOSSRED and SWMPLOT.	97
APPENDIX II. Program GVAL.	142
APPENDIX III. Program QSPLIT.	147
APPENDIX IV. Program RELAX	154
APPENDIX V. Program MULTEPR	175
APPENDIX VI. Program MOSSFIT	186

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Transition probability amplitudes C_{nm}^{LM} for nuclear spins $I^g = 1/2$ and $I^e = 3/2$ with M1 and E2 character	39
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 paramters	50
3	All permutations of the g tensor yielding real eigenvectors, the coefficients of the eigenvector and crystal field parameters for LOW model complex	52
4	Mossbauer parameters for the three components RLX, IMP, and HI on Fe(TPP)(S ϕ)(HS ϕ) at selected temperatures	68
5	Crystal field parameters and wave function coefficients calculated from EPR g tensor for LOW and P-450	79
6	Parameters used in simulating Mossbauer spectra for P-450 and LOW	83

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Reaction cycle of cytochrome P450 in the bacteria <u>Pseudomonas putida</u>	3
2	Five coordinate and six coordinate forms of Fe(III) TPP(S ϕ)(HS ϕ) distances in angstroms . .	7
3	Cross-sectional view of sample area of magnetic susceptibility apparatus	12
4	Tanabe-Sugano diagram for d ⁵ electron configuration in an octahedral crystal field . . .	15
5	Mossbauer spectra of Fe(TPP)(S ϕ)(HS ϕ) as a function of temperature	59
6	Temperature dependent Mossbauer spectra of Fe(TPP)(S ϕ)(HS ϕ)	60
7	Temperature dependent Mossbauer spectra of Fe(TPP)(S ϕ)(HS ϕ)	61
8	Temperature dependent Mossbauer spectra of SRL14 both in and out of a magnetic field . . .	62
9	Temperature dependent Mossbauer spectra of SRL2 allowed to decompose on air.	63
10	Effective magnetic moment of SRL12 as a function of temperature	65
11	EPR spectra of SRL12 as a function of temperature	66
12	Difference spectrum of selected Mossbauer spectra at the same temperature	70
13	Mossbauer spectra of a sample both in and out of a polarizing magnetic field.	73
14	Simulated EPR spectrum of the low-spin contribution (LOW) of Fe(TPP)(S ϕ)(HS ϕ)	79
15	RLX using parameters from Table 6 as a function of the relaxation rate constant VJ2. . . .	83
16	The three components which are summed to simulate the spectra of Fe(TPP)(HS ϕ)(S ϕ)	84

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^O) 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^{OS}). The resulting enzyme-substrate complex accepts an electron and is reduced to a high spin ferrous species (m^{rs}). Molecular oxygen then binds to the ferrous species yielding a nonparamagnetic species ($m_{O_2}^{rs}$). 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

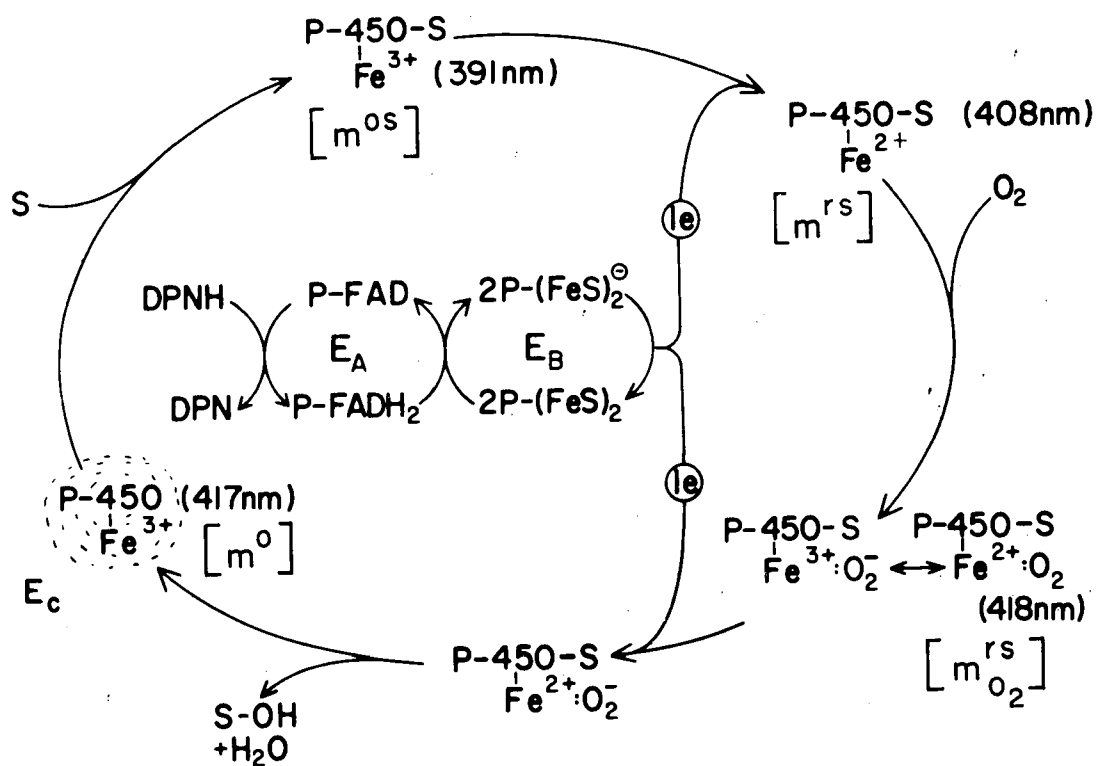


Figure 1. Reaction cycle of cytochrome P450 in the bacteria *Pseudomonas putida* (from Ref. [2]).

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 $\text{Fe}^{\text{III}} - \text{O}_2^-$ 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, $\text{Fe}(\text{TPP})(\text{C}_6\text{H}_5\text{S})(\text{C}_6\text{H}_5\text{SH})$ 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.

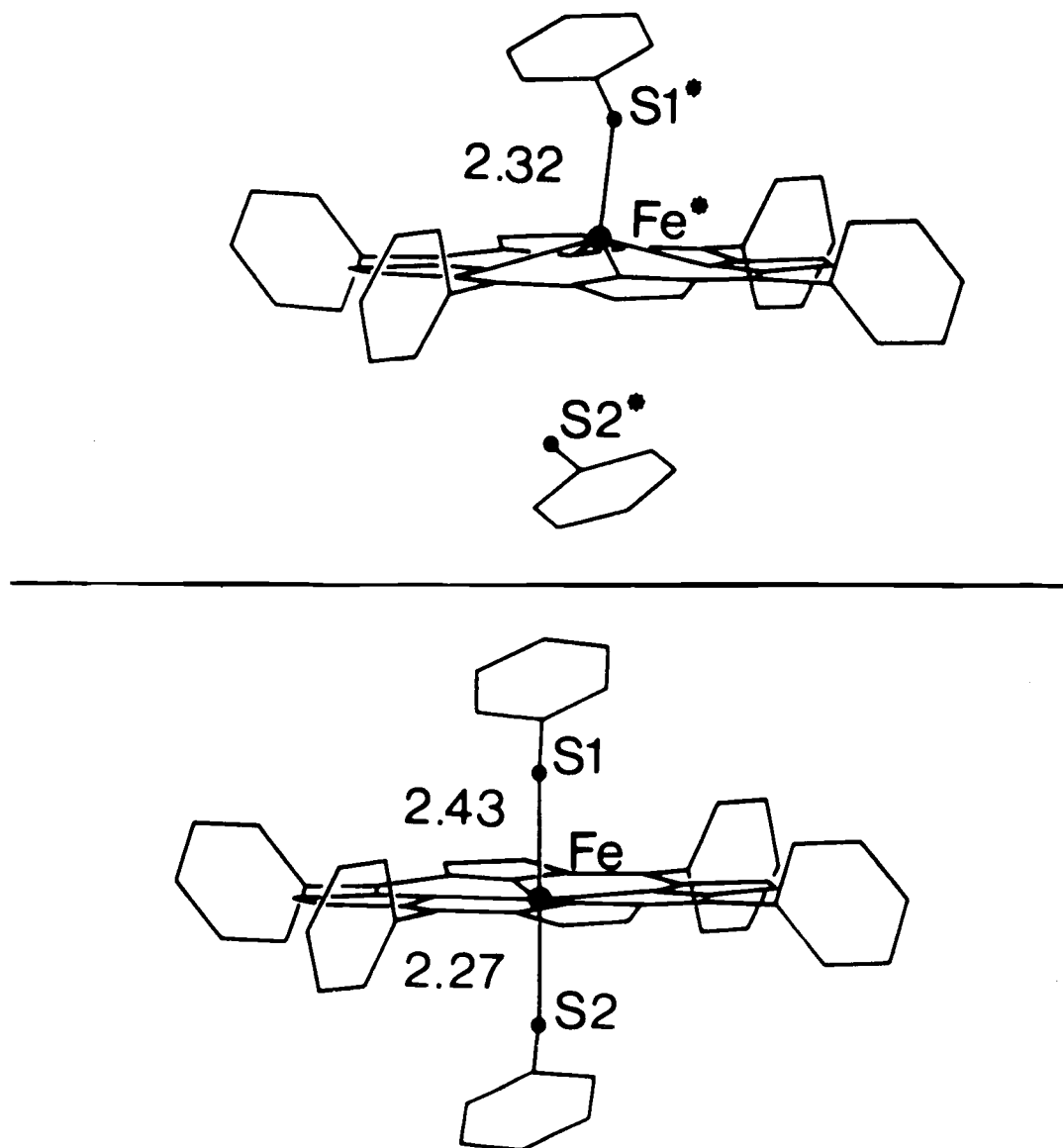


Figure 2. Five coordinate (top) and six coordinate forms of $\text{Fe(III) TPP(S}\phi\text{)(HS}\phi\text{)}$ distances in angstroms (from Ref. [15]).

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 mesotetra-phenylporphyrin iron (III) μ -oxo dimer was dissolved in 70 ml benzene and stirred for one hour with 75 ml of 15% H_2SO_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 $\text{Fe}(\text{TPP})(\text{S}\phi)(\text{HS}\phi)$ 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:

Sample	%C	%H	%N	%Fe	%S
SRL 12	76.00	4.40	6.34	6.34	6.99
SRL 14	75.49	4.47	6.38	6.40	7.00
Theory	75.76	4.40	6.31	6.30	7.23

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_{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^{-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.

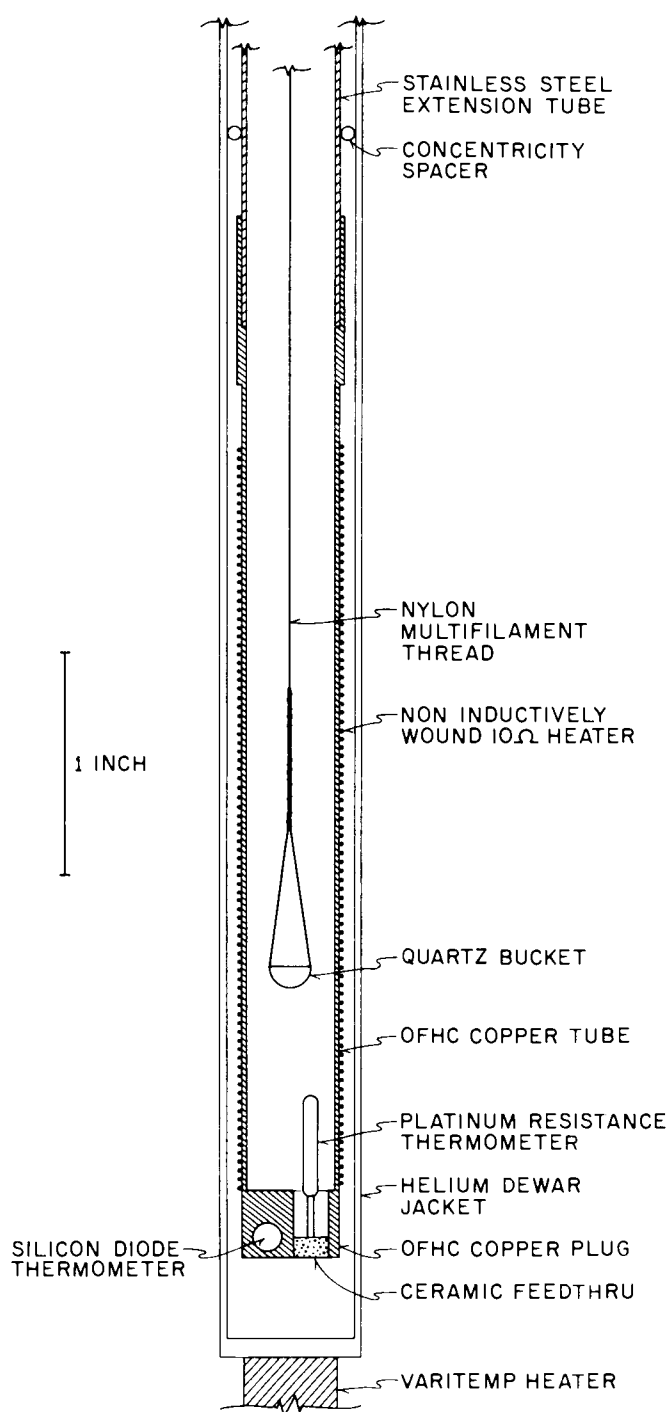


Figure 3. Cross-sectional view of sample area of magnetic susceptibility apparatus.

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 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.

$$\mathcal{H}_{CF} = -e \sum_k v(\vec{r}_k) \quad (3)$$

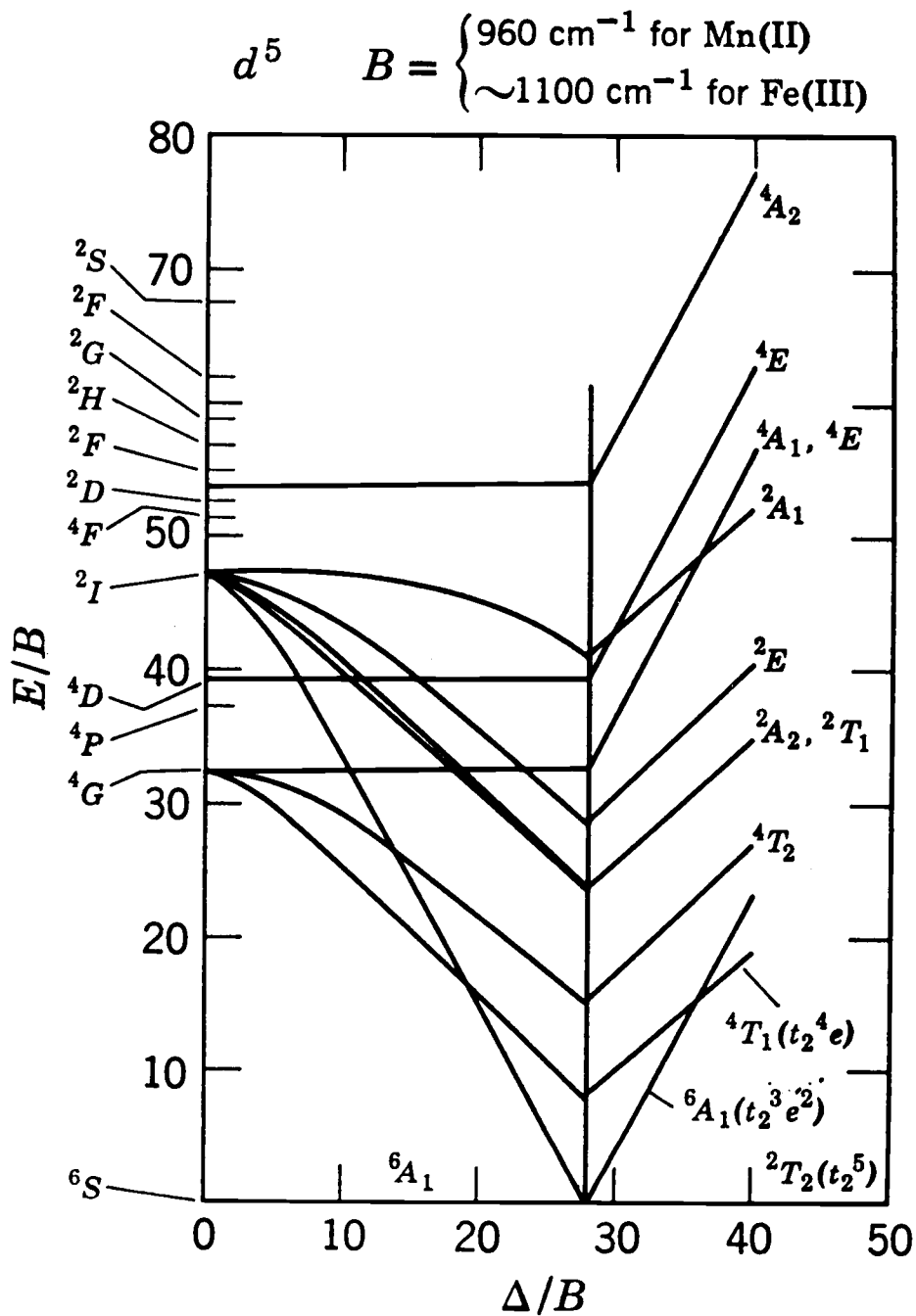


Figure 4. Tanabe-Sugano diagram for d^5 electron configuration in an octahedral crystal field (from Ref. [37]). Δ is the crystal field strength, B is interelectronic repulsion strength, and E is the energy relative to the ground state energy.

is the interaction of the atomic electrons with the crystal field potential $V(\vec{r})$.

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

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

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

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

$$\begin{aligned} \mathcal{H}_{MHFS} = 2g_n\beta_n\beta \sum_k \left[\left\{ \frac{(\vec{l}_k + \vec{s}_k)}{r_k^3} + \frac{3(\vec{r}_k \cdot \vec{s}_k)(\vec{r}_k)}{r_k^3} \right\} \right. \\ \left. + \frac{8\pi}{3} \delta(\vec{r}_k) \cdot \vec{s}_k \right] \cdot \vec{I} \end{aligned} \quad (6)$$

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.

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

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

$$\mathcal{H}_{HN} = -g_n\beta_n \vec{H}_O \cdot \vec{I} \quad (8)$$

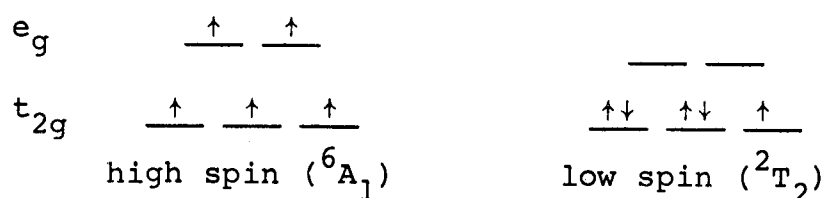
is the interaction between the nucleus and an external magnetic field. The general forms of the operators are given here to show the full operator and will be discussed in subsequent sections.

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 $\mathcal{H}_{CF} \gg \mathcal{H}_C$, 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.



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 (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 ΔE , 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 2T_2 ground state term for Fe^{III} .

Since the 2T_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 2T_2 .

Instead of working with the complex five electron wave function represented by 2T_2 , it is convenient to think of the configuration t_{2g}^5 as a hole in a complete t_{2g}^6 system [44]. The hole configuration is then isomorphous with the one electron orbitals commonly denoted $|XY\rangle$, $|YZ\rangle$, and $|XZ\rangle$ which, in terms of spherical harmonics [45], are given by

$$\begin{aligned} |XY\rangle &= \frac{1}{\sqrt{2}} (Y_2^2 - Y_2^{-2}) \\ |XZ\rangle &= \frac{1}{i\sqrt{2}} (Y_2^1 - Y_2^{-1}) \\ |YZ\rangle &= \frac{1}{\sqrt{2}} (Y_2^1 + Y_2^{-1}) \end{aligned} \quad (9)$$

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

$$\begin{aligned} |XY\rangle &= \frac{1}{\sqrt{2}} (|2, 2\rangle - |2, -2\rangle) = |\zeta\rangle \\ |XZ\rangle &= \frac{1}{i\sqrt{2}} (|2, 1\rangle - |2, -1\rangle) \\ |YZ\rangle &= \frac{1}{\sqrt{2}} (|2, 1\rangle + |2, -1\rangle) \end{aligned} \quad (10)$$

It is often convenient to work in a basis of near angular momentum eigenfunctions (dropping the $\ell = 2$ from our states for simplicity) given by

$$\begin{aligned} |1\rangle &= -\frac{1}{\sqrt{2}} (|YZ\rangle - i|XZ\rangle) \\ |-1\rangle &= -\frac{1}{\sqrt{2}} (|YZ\rangle + i|XZ\rangle) \\ |\zeta\rangle &= |XY\rangle \end{aligned} \quad (11)$$

The t_{2g}^5 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 $|1\rangle\alpha$ would denote electrons in the $|1\rangle\beta$, $|-1\rangle\alpha$, $|-1\rangle\beta$, $|\zeta\rangle\alpha$ and $|\zeta\rangle\beta$ states, where α and β 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

$$\begin{aligned} \mathcal{H}_{CF} + \mathcal{H}_{SO} &= D[\ell_z^2 - \ell(\ell+1)/3] + E[\ell_x^2 - \ell_y^2] - \lambda(\bar{\ell} \cdot \bar{s}) \\ &= D[\ell_z^2 - \ell(\ell+1)/3] + \frac{E}{2}[\ell_+^2 + \ell_-^2] - \lambda(\bar{\ell} \cdot \bar{s}) \end{aligned} \quad (12)$$

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

	$ 1\rangle\alpha$	$ \zeta\rangle\beta$	$ -1\rangle\alpha$	$ -1\rangle\beta$	$- \zeta\rangle\alpha$	$ 1\rangle\beta$
$\langle 1 \alpha$	$-D-\lambda/2$	$-\lambda/\sqrt{2}$	$3E$	0	0	0
$\langle \zeta \beta$	$-\lambda/\sqrt{2}$	$2D$	0	0	0	0
$\langle -1 \alpha$	$3E$	0	$-D+\lambda/2$	0	0	0
$\langle -1 \beta$	0	0	0	$-D-\lambda/2$	$-\lambda/\sqrt{2}$	$3E$
$-\langle \zeta \alpha$	0	0	0	$-\lambda/\sqrt{2}$	$2D$	0
$\langle 1 \beta$	0	0	0	$3E$	0	$-D+\lambda/2$

(13)

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

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

and (14)

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

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:

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

and (15)

$$|\psi_i^-\rangle = A_i^* |YZ\rangle\beta - B_i^* |XY\rangle\alpha - C_i^* |XZ\rangle\beta \quad i=1,2,3$$

where $A' = -(A + C)/\sqrt{2}$

$$B' = B$$

$$C' = i(A - C)/\sqrt{2}$$

The Zeeman interaction, expressed as an angular momentum operator by $\beta \bar{H} \cdot (2\bar{s} + k\bar{l})$, 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.

$$\mathcal{H}_Z = \beta \bar{H} \cdot (2\bar{s} + k\bar{l}) = \beta \cdot \bar{H} \cdot \tilde{g} \cdot \bar{S}_{\text{eff}} \quad (16)$$

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

$$|-\frac{1}{2}\rangle = |\psi^-\rangle$$

(17)

so when we equate the corresponding matrix elements

$$\langle \frac{1}{2} | \beta H_z g_z S_{\text{eff},z} | \frac{1}{2} \rangle = \langle \psi^+ | \beta H_z (k l_z + 2S_z) | \psi^+ \rangle \quad (18)$$

we find

$$(1/2)g_z = A^2 - B^2 + C^2 + k(A^2 - C^2)$$

Summarizing, we have [47]

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

which, if k is unity, simplifies to [44]

$$\begin{aligned} g_x &= 2(\sqrt{2}A + B)(\sqrt{2}C - B) \\ g_y &= 2(\sqrt{2}A + B)(\sqrt{2}C + B) \\ g_z &= 2(\sqrt{2}A + B)(\sqrt{2}A - B) \end{aligned} \quad (20)$$

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]:

$$\mathcal{H}_{\text{CF}} = D(S_z^2 - S(S+1)/3 + E(S_x^2 - S_y^2)) \quad (21)$$

The first term is the axial crystal field distortion and the second term is the rhombic distortion. The basis wavefunctions are given by $|S, S_z\rangle$. For $S = 5/2$, they are $|5/2, \pm 5/2\rangle$, $|5/2, \pm 3/2\rangle$, and $|5/2, \pm 1/2\rangle$. The 6×6 matrix of this interaction, in block diagonal form, is (omitting the S for simplicity)

	$ 5/2\rangle$	$ 1/2\rangle$	$ -3/2\rangle$	$ -5/2\rangle$	$ -1/2\rangle$	$ 3/2\rangle$	
$\langle 5/2 $	$10D/3$	$10E$	0	0	0	0	
$\langle 1/2 $	$10E$	$-8D/3$	$3\sqrt{2}E$	0	0	0	
$\langle -3/2 $	0	$3\sqrt{2}E$	$-2D/3$	0	0	0	
$\langle -5/2 $	0	0	0	$10D/3$	$10E$	0	(22)
$\langle -1/2 $	0	0	0	$10E$	$-8D/3$	$3\sqrt{2}E$	
$\langle 3/2 $	0	0	0	0	$3\sqrt{2}E$	$-2D/3$	

Diagonalization of this matrix yields three doubly degenerate eigenstates given by

$$|\psi_i^\pm\rangle = a_i |\pm 5/2\rangle + b_i |\pm 1/2\rangle + c_i |\mp 3/2\rangle \quad i=1,2,3 \quad (23)$$

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

$$\begin{aligned} g_{x,i} &= g_J (3b_i^2 + 2\sqrt{5}a_i c_i + 4\sqrt{2}b_i c_i) \\ g_{y,i} &= (-1)^{i+1} g_J (3b_i^2 + 2\sqrt{5}a_i c_i - 4\sqrt{2}b_i c_i) \\ g_{z,i} &= (-1)^{i+1} 2g_J (5/2 a_i^2 + 1/2 b_i^2 - 3/2 c_i^2) \end{aligned} \quad (24)$$

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 λ . 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

$$\mathcal{H} = \frac{eQ}{2I(2I-1)} (V_{zz}I_z^2 + V_{xx}I_x^2 + V_{yy}I_y^2) - g_n B_n \bar{I} \cdot \bar{H} \quad (25)$$

where the first term is the electric quadrupole interaction, and the second term is the magnetic hyperfine interaction, with \bar{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 3×3 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

$$V_{xx} + V_{yy} + V_{zz} = 0. \quad (26)$$

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

$$eq = V_{zz}$$

and

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (27)$$

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

$$H_Q = \frac{e^2 q Q}{12} \left[3I_z^2 - \frac{15}{4} + \eta (I_x^2 - I_y^2) \right]$$

or

(28)

$$H_Q = \frac{e^2 q Q}{4} \left[I_z^2 - 5/4 + \eta/6 (I_+^2 + I_-^2) \right]$$

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

$$\Delta E = \frac{e^2 q Q}{2} (1 + \eta^2/3)^{1/2} \quad (29)$$

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

$$q = (1 - R)q_{\text{val}} + (1 - \gamma_{\infty})q_{\text{latt}} = V_{zz}/e \quad (30)$$

$$\eta q = (1 - R)\eta q_{\text{val}} + (1 - \gamma_{\infty})\eta q_{\text{latt}} = (V_{xx} - V_{yy})/e \quad (31)$$

where q_{val} and q_{latt} are the valence and lattice contribution to the EFG and $(1 - R)$ and $(1 - \gamma_{\infty})$ 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

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

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

$$\hat{q}_{val} = \frac{V_{zz}}{e} = \frac{3z^2 - r^2}{r^2} = \left(\frac{16\pi}{5}\right)^{1/2} Y_2^0 \langle r^{-3} \rangle \quad (32)$$

and

$$\begin{aligned} \eta \hat{q}_{val} &= \frac{V_{xx} - V_{yy}}{e} = \frac{3}{2} \frac{x^2 - y^2}{r^5} \\ &= \frac{3}{2} \left(\frac{32\pi}{15}\right)^{1/2} \langle r^{-3} \rangle [Y_2^2 + Y_2^{-2}] \end{aligned} \quad (33)$$

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 $|XY\rangle$, $|XZ\rangle$, $|YZ\rangle$

$$|\psi^+\rangle = C_1 |XY\rangle\beta + C_2 |XZ\rangle\alpha + C_3 |YZ\rangle\alpha \quad (34)$$

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

$$\begin{aligned} \langle \psi^+ | \hat{q}_{val} | \psi^+ \rangle &= \frac{2}{7} \langle r^{-3} \rangle \left[\frac{1}{2} (A^2 + C^2) (N_{xz}^2 + N_{yz}^2) - 2B^2 (N_{xy}^2) \right. \\ &\quad \left. + AC (N_{yz}^2 - N_{xz}^2) \right] \end{aligned} \quad (35)$$

and

$$\langle \psi^+ | \eta \hat{q}_{val} | \psi^+ \rangle = \frac{6}{7} \langle r^{-3} \rangle \left[\frac{1}{2} (A^2 + C^2) (N_{xz}^2 - N_{yz}^2) - AC (N_{yz}^2 + N_{xz}^2) \right] \quad (36)$$

rearranging gives

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

However, these matrix elements only give the contribution to the EFG from one of the eigenstates. To find q_{val}

and η_{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]

$$q_{\text{val}} = \frac{\sum_{i=1,3} \langle \psi_i^+ | \hat{q}_{\text{val}} | \psi_i^+ \rangle e^{-(E_i - E_1)/kT}}{\sum_{i=1,3} \langle \psi_i^+ | \psi_i^+ \rangle e^{-(E_i - E_1)/kT}} \quad (38)$$

and

$$\eta q_{\text{val}} = \frac{\sum_{i=1,3} \langle \psi_i^+ | \eta \hat{q}_{\text{val}} | \psi_i^+ \rangle e^{-(E_i - E_1)/kT}}{\sum_{i=1,3} \langle \psi_i^+ | \psi_i^+ \rangle e^{-(E_i - E_1)/kT}} \quad (39)$$

where $|\psi_i^+\rangle$ 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

$$\mathcal{H}_{\text{MHFS}} = -g_n \beta_n \vec{I} \cdot \vec{H} \quad (40)$$

where g_n is the nuclear gyromagnetic ratio ($g_n = 0.1806$, -0.1033 for the ground and first excited states

respectively) and β_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 [47]

$$\mathcal{H}_{\text{MHFS}} = P(\bar{\mathbf{L}} \cdot \bar{\mathbf{I}} - \kappa \bar{\mathbf{S}} \cdot \bar{\mathbf{I}} + \frac{1}{7} \sum_{k=1}^n \bar{\mathbf{a}}_k \cdot \bar{\mathbf{I}}) - g_n \beta_n \bar{\mathbf{I}} \cdot \bar{\mathbf{H}}_{\text{ext}} \quad (41)$$

where

$$\bar{\mathbf{a}}_k = 4\bar{\mathbf{s}}_k - (\bar{\mathbf{l}}_k \cdot \bar{\mathbf{s}}_k) \bar{\mathbf{l}}_k - \bar{\mathbf{l}}_k (\bar{\mathbf{l}}_k \cdot \bar{\mathbf{s}}_k) \quad (42)$$

and

$$P = 2g_n \beta_n \beta \langle r^{-3} \rangle_{\text{eff}} \quad (43)$$

In these equations: β = electron magneton; $\bar{\mathbf{L}}$ is the total angular momentum which is a vector sum of the angular momentum, $\bar{\mathbf{l}}_k$ for all the k electrons; $\bar{\mathbf{S}}$ is the total spin, and also a vector sum over the individual electron spins $\bar{\mathbf{s}}_k$. 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 κ , 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, κ , is analogous [7] to the k term used in calculating the g tensor. The $\langle r^{-3} \rangle_{\text{eff}}$ 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

$$\mathcal{H}_{\text{MHFS}} = \vec{I} \cdot \vec{A} \cdot \vec{S} \quad (44)$$

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 κ . Using table A-41 of Griffith [47] to help evaluate Eq. (42), and the wavefunction of Eq. (14) we find [53]

$$\begin{aligned}
A_x &= P[2\sqrt{2}B(C-A) - \kappa(2AC-B^2) - \frac{1}{7}(2B^2+6C^2-3\sqrt{2}AB+2AC-3\sqrt{2}BC)] \\
A_y &= P[2\sqrt{2}B(C+A) - \kappa(2AC+B^2) - \frac{1}{7}(-2B^2-6C^2+3\sqrt{2}AB+2AC-3\sqrt{2}BC)] \\
A_z &= P[2(A^2-C^2) - \kappa(A^2-B^2+C^2) + \frac{2}{7}(1+B^2-3\sqrt{2}AB)]
\end{aligned} \tag{45}$$

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

$$\begin{aligned}
A_x &= \frac{P}{2}[8C_1C_2i - 2\kappa(-C_1^2+C_2^2+C_3^2) + \frac{2}{7}(-2C_1^2+2C_2^2-4C_3^2-6C_1C_3+6iC_2C_3)] \\
A_y &= \frac{P}{2}[-8C_1C_3 - 2\kappa(C_1^2+C_2^2+C_3^2) + \frac{2}{7}(2C_1^2-4C_2^2+2C_3^2+6C_1C_3-6iC_2C_3)] \\
A_z &= P[4C_2C_3i + \kappa(C_1^2+C_2^2-C_3^2) - \frac{2}{7}(-2C_1^2+C_2^2-C_3^2-3iC_1C_2-3C_1C_3)]
\end{aligned} \tag{46}$$

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

$$H = H_{MHS} = A \cdot \bar{I} \cdot \langle S \rangle_{\text{eff}} + g_n \beta_n \bar{I} \cdot \bar{H}_{\text{ext}} \tag{47}$$

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

$$I(\omega) = \text{Re}[F(p)] \quad (48)$$

where

$$F(p) = \sum_{\text{all indices}} \langle \mu n | M_{LM}^+ | \nu m \rangle \langle \mu n \nu m | \bar{U} | \mu' n' \nu' m' \rangle \langle \nu' m' | M_{LM} | \mu' n' \rangle \quad (49)$$

M_{LM} is an electromagnetic multipole operator of multipolarity L and polarization M which induces transitions between various hyperfine levels.

The superoperator \bar{U} contains the physical information about the system and is defined by the total Hamiltonian \mathcal{H}_0 , for the electron-nuclear system. Its matrix elements can be defined by the quantum mechanical time average of the evolution operator

$$\exp[i\int_0^t \mathcal{H}_0(t') dt'] = \bar{\Gamma}(t) \quad (50)$$

$$(\langle \mu n | \bar{\Gamma}(t) | \mu' n' \rangle \langle \nu m | \bar{\Gamma}^\dagger(t) | \nu' m' \rangle)_{\text{ave}} \equiv \langle \mu n \nu m | \bar{U} | \mu' n' \nu' m' \rangle$$

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 \underline{U} which is readily defined in various approximations and which satisfies

$$\bar{U} = \underline{U}^{-1} \equiv [p\tilde{I} - \frac{i}{\hbar} \mathcal{H}_0^X - R]^{-1} \quad (51)$$

with $p = \Gamma - i\omega$, Γ the natural linewidth of the resonance line, \mathcal{H}_0^X 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^XB gives the commutator of A and B.

$$A^XB = [A, B] = AB - BA \quad (52)$$

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

$$\mathcal{H}|\nu\rangle = E_\nu |\nu\rangle \quad (53)$$

and

$$\mathcal{H}|\mu\rangle = E_\mu |\mu\rangle$$

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

$$\mathcal{H}^X |\mu\rangle\langle\nu| = \mathcal{H}|\mu\rangle\langle\nu| - |\mu\rangle\langle\nu|\mathcal{H} = (E_\mu - E_\nu) |\mu\rangle\langle\nu| \quad (54)$$

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

$$\langle\mu\nu|A^X|\mu'\nu'\rangle = \delta_{\nu\nu'}\langle\mu|A|\mu'\rangle - \delta_{\mu\mu'}\langle\nu'|A|\nu\rangle \quad (55)$$

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_z^g , the electronic spin S_z^g when the nucleus is in the ground state, and the corresponding spins in the excited state I_z^e and S_z^e . Thus, the basis vector is given by $|\mu\nu m\rangle = |S_z^g I_z^g S_z^e I_z^e\rangle$.

Let us now examine each term of Eq. (49). The terms involving M_{LM}^+ and 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

$$\langle \nu' m' | M_{LM} | \mu' n' \rangle = \delta_{\nu' \mu'} C_{m' n'}^{LM}$$

and

(56)

$$\langle \mu n | M_{LM}^+ | \nu m \rangle = \delta_{\mu \nu} (C_{nm}^{LM})^+$$

where C_{mn}^{LM} 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

$$F(p) = \sum_{\text{all indices}} (C_{mn}^{LM})^+ (C_{m' n'}^{LM}) \langle \mu \nu m | \underline{U}^{-1} | \mu' n' \nu' m' \rangle \quad (57)$$

Table 1. Transition probability amplitudes C_{nm}^{LM} for nuclear spins $I^g = 1/2$ and $I^e = 3/2$ with M1 and E2 character (from Ref. 59).

n	m	M	L=1	L=2
1/2	3/2	1	$\sqrt{3/12}$	$\sqrt{1/20}$
1/2	1/2	0	$\sqrt{2/12}$	$\sqrt{2/20}$
1/2	-1/2	-1	$\sqrt{1/12}$	$\sqrt{3/20}$
1/2	-3/2	-2	0	$\sqrt{4/20}$
-1/2	3/2	2	0	$-\sqrt{4/20}$
-1/2	+1/2	1	$\sqrt{1/12}$	$-\sqrt{3/20}$
-1/2	-1/2	0	$\sqrt{2/12}$	$-\sqrt{2/20}$
-1/2	-3/2	-1	$\sqrt{3/12}$	$\sqrt{1/20}$

In matrix notation, this becomes

$$F_{(p)} = \sum_{LM} (C^{LM})^+ \underline{U}^{-1} (C^{LM}) \quad (58)$$

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

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

$$\mathcal{H}_0 = \mathcal{H}_Q + \mathcal{H}_{MHFS} \quad (59)$$

and have matrix elements of the form

$$\begin{aligned} \langle \mu n v m | \mathcal{H}_0^x | \mu' n' v' m' \rangle &= \delta_{vv'} \delta_{mm'} \langle \mu n | \mathcal{H}_{MHFS} | \mu' n' \rangle \\ &- \delta_{\mu\mu'} \delta_{nn'} \langle v' m' | \mathcal{H}_Q^* + \mathcal{H}_{MHFS}^* | v m \rangle \end{aligned} \quad (60)$$

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

$$\tilde{A}/g_n = \tilde{A}^*/g_n^* \quad (61)$$

Since \mathcal{H}_Q is zero for the ground state, it does not contribute to \mathcal{H}_0 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 $\bar{H}(t)$ set up by the bath

$$\mathcal{H} = \bar{S} \cdot \tilde{\alpha} \cdot \bar{H}(t) \quad (62)$$

If the interaction is assumed to be a true magnetic type, as in the common spin-spin interaction, then $\tilde{\alpha} = \tilde{g}\beta$ where \tilde{g} is the gyromagnetic g tensor of Eq. (19). The relaxation operator \hat{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 $\bar{H}(t)$. If it is assumed that $J_q(\omega) \approx J_q(0) \equiv J_q$ and that $\bar{H}(t)$ is isotropic, then a relaxation rate W_i , ($i = x, y, z$) can be defined.

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

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

$$\begin{aligned} & \langle \mu\nu m | \hat{R} | \mu' n' v' m' \rangle \\ &= \delta_{nn'} \delta_{mm'} \{ \delta_{\mu\mu'} \delta_{vv'} [W_z (2 \langle v | S_z | v' \rangle \langle \mu' | S_z | \mu \rangle - \frac{1}{2}) - \frac{1}{2} (W_x + W_y)] \\ &+ [\frac{1}{2} (W_x + W_y)] [\langle v | S_+ | v' \rangle \langle \mu' | S_- | \mu \rangle + \langle v | S_- | v' \rangle \langle \mu' | S_+ | \mu \rangle] \quad (64) \\ &+ [\frac{1}{2} (W_x - W_y)] [\langle v | S_+ | v' \rangle \langle \mu' | S_+ | \mu \rangle + \langle v | S_- | v' \rangle \langle \mu' | S_- | \mu \rangle] \} \end{aligned}$$

Using the above and a procedure suggested by Clauser [60], the Mossbauer spectra can now be calculated. By obtaining the eigenvalues $\bar{\lambda}$ and the eigenvectors \bar{V} of \bar{U} for

the case $\omega = 0$, then (49) can be re-expressed as

$$F(p) = \sum_m (M_{LM}^+ \cdot \bar{V}) (\bar{\lambda} - i\omega\bar{I})^{-1} (\bar{V}^{-1} \cdot M_{LM}) \quad (65)$$

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, 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" ($\Omega_S \sim \Omega_L = g_n \beta_n H_{int}/\hbar$) and lead to ill-resolved hyperfine structure. However, if a polarizing field of sufficient strength ($H_{ext} > 15$ 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 $\langle S \rangle$ ion, the size of H_{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 α and β with + and - to denote spin, we have

$$|\psi_i^{\pm}\rangle = A_i |\pm 1^{\pm}\rangle \pm B_i |\zeta^{\mp}\rangle + C_i |\mp 1^{\pm}\rangle \quad (14)$$

where, when k is unity, has g values

$$\begin{aligned}
g_x &= 2(\sqrt{2}A + B)(\sqrt{2}C - B) \\
g_y &= 2(\sqrt{2}A + B)(\sqrt{2}C + B) \\
g_z &= 2(\sqrt{2}A + B)(\sqrt{2}A - B)
\end{aligned} \tag{20}$$

If we assume k is unity, it can be shown that [61]

$$\begin{aligned}
A &= (2g_x + g_y - g_z)/4(g_z + g_y - g_x)^{1/2} \\
B &= (g_y - g_x)/2(2(g_z + g_y - g_x))^{1/2} \\
C &= (g_y + g_x)/4(g_z + g_y - g_x)^{1/2}
\end{aligned} \tag{66}$$

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

$$\frac{g_x^2 + g_y^2 + g_z^2 + g_y g_z - g_x g_y - g_x g_z}{4(g_y + g_z + g_x)} = 1 \tag{67}$$

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

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

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

$$\bar{f}(\bar{x}) = \bar{0} \quad (68)$$

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

$$0 = \bar{f}(\bar{a}) + (\widetilde{\text{grad } f}) \cdot \bar{\Delta} . \quad (69)$$

After solving this set of equations for the vector $\bar{\Delta}$, the new approximation to the solution is given by

$$\bar{B} = \bar{A} + \bar{\Delta} \quad (70)$$

This is continued until either the method has converged to give a very small $\bar{\Delta}$ 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

$$\begin{aligned}
 0 &= g_x(A, B, C, k) - g'_x \\
 0 &= g_y(A, B, C, k) - g'_y \\
 0 &= g_z(A, B, C, k) - g'_z \\
 0 &= A^2 + B^2 + C^2 - 1
 \end{aligned}
 \tag{71}$$

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 \bar{I} , we can plug into

$$\begin{aligned}
 0 &= g_x(\bar{I}) - g'_x + \frac{\partial g_x(\bar{I})}{\partial A} \Delta A + \frac{\partial g_x(\bar{I})}{\partial B} \Delta B + \frac{\partial g_x(\bar{I})}{\partial C} \Delta C + \frac{\partial g_x(\bar{I})}{\partial k} \Delta k \\
 0 &= g_y(\bar{I}) - g'_y + \frac{\partial g_y(\bar{I})}{\partial A} \Delta A + \frac{\partial g_y(\bar{I})}{\partial B} \Delta B + \frac{\partial g_y(\bar{I})}{\partial C} \Delta C + \frac{\partial g_y(\bar{I})}{\partial k} \Delta k \\
 0 &= g_z(\bar{I}) - g'_z + \frac{\partial g_z(\bar{I})}{\partial A} \Delta A + \frac{\partial g_z(\bar{I})}{\partial B} \Delta B + \frac{\partial g_z(\bar{I})}{\partial C} \Delta C + \frac{\partial g_z(\bar{I})}{\partial k} \Delta k \\
 0 &= A^2 + B^2 + C^2 - 1 + 2A \cdot \Delta A + 2B \Delta B + 2C \Delta C + 0
 \end{aligned}
 \tag{72}$$

The correction vector $\bar{\Delta}$ to the estimate vector \bar{I} is given by $\bar{\Delta} = (\Delta A, \Delta B, \Delta C, \Delta k)$, 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 1×10^{-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 $H\psi = E_1\psi$ as determined earlier gives three equations and three unknowns, from (13),

$$\begin{aligned} E_1/\lambda + D/\lambda - 3EC/\lambda A &= -1/2 - B/\sqrt{2}A \\ E_1/\lambda - 2D/\lambda &= -A/\sqrt{2}B \\ E_1/\lambda + D/\lambda - 3EA/\lambda C &= 1/2 \end{aligned} \quad (73)$$

This set of equations can then be solved to obtain D/λ and E/λ , the crystal field parameters, and E_1/λ , 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 λ , 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.

GX	GY	GZ	ANORM	A	B	C	K	D/LAM	E/LAM	E/D	ENERGY/LAM
1.921	2.249	2.417	1.007521	.769677	.062580	.635360	1.146313	1.9590899	-.9134092	-.4662416	-4.7786101
1.921	2.417	2.249	1.007521	.746769	.094976	.658267	1.146313	.3905688	-1.4362495	-3.6773279	-4.7786101
-1.921	2.249	2.417	1.100249	.837037	.546210	.031992	1.150917	.0400138	-.0186463	-.4659956	-1.0035754
-1.921	2.249	-2.417	1.259494	-.948811	.314569	-.028353	-2.235386	-.7996812	-.0076326	.0095446	.5334313
-1.921	-2.249	2.417	1.134158	.251199	.634346	.731098	-2.149518	.3842966	.3617462	.9413203	.4885816
-1.921	2.417	2.249	1.100249	.820744	.569253	.049286	1.150917	.0079625	-.0293300	-3.6835276	-1.0035754
-1.921	2.417	-2.249	1.134158	.939699	-.339340	.042598	-2.149518	-.7347675	-.0112752	.0153453	.4885816
-1.921	-2.417	2.249	1.259494	-.266148	-.650862	-.711016	-2.235386	.4112896	.3960243	.9628844	.5334313
2.249	1.921	2.417	1.134158	.251199	.634346	-.731098	-2.149518	.3842966	-.3617462	-.9413203	.4885816
2.249	2.417	1.921	1.134158	.208601	.694589	-.688500	-2.149518	.3504710	-.3730214	-1.0643431	.4885816
-2.249	1.921	2.417	1.100249	.837037	.546210	-.031992	1.150917	.0400138	.0186463	.4659956	-1.0035754
-2.249	1.921	-2.417	1.259494	-.948811	.314569	.028353	-2.235386	-.7996812	.0076326	-.0095446	.5334313
-2.249	-1.921	2.417	1.007521	.769677	.062580	-.635360	1.146313	1.9590899	.9134092	.4662416	-4.7786101
-2.249	2.417	1.921	1.100249	.788751	.614497	.016294	1.150917	-.0479763	-.0106838	.2226886	-1.0035754
-2.249	2.417	-1.921	1.007521	.111409	.993511	.022908	1.146313	-2.3496587	-.5228404	.2225176	-4.7786101
-2.249	-2.417	1.921	1.259494	-.237795	-.690960	-.682663	-2.235386	.3883917	.4036569	1.0393038	.5334313
2.417	1.921	2.249	1.259494	-.266148	-.650862	.711016	-2.235386	.4112896	-.3960243	-.9628844	.5334313
2.417	2.249	1.921	1.259494	-.237795	-.690960	.682663	-2.235386	.3883917	-.4036569	-1.0393038	.5334313
-2.417	1.921	2.249	1.100249	.820744	.569253	-.048286	1.150917	.0079625	.0293300	3.6835276	-1.0035754
-2.417	1.921	-2.249	1.134158	.939699	-.339340	-.042598	-2.149518	-.7347675	.0112752	-.0153453	.4885816
-2.417	-1.921	2.249	1.007521	.746769	.094976	-.658267	1.146313	.3905688	1.4362495	3.6773279	-4.7786101
-2.417	2.249	1.921	1.100249	.788751	.614497	-.016294	1.150917	-.0479763	.0106838	-.2226886	-1.0035754
-2.417	2.249	-1.921	1.007521	.111409	.993511	-.022908	1.146313	-2.3496587	.5228404	-.2225176	-4.7786101
-2.417	-2.249	1.921	1.134158	.208601	.694589	.688500	-2.149518	.3504710	.3730214	1.0643431	.4885816

Table 3. All permutations of the g tensor yielding real eigenvectors, the coefficients of the eigenvector and crystal field parameters for LOW model complex.

GX	GY	GZ	ANORM	A	B	C	K	D/LAM	E/LAM	E/D	ENERGY/LAM
1.965	2.240	2.363	1.015051	.746676	.040153	.663975	1.583424	2.8961151	-1.4704265	-.5077238	-7.3568348
1.965	2.363	2.240	1.015051	.733718	.058478	.676933	1.583424	.7575822	-2.1832708	-2.8818930	-7.3568348
-1.965	2.240	2.363	1.096247	.832771	.552966	.026848	1.144712	.0312855	-.0158085	-.5052988	-1.0023381
SOLVING FOR A,B,C,AND K FAILED TO CONVERGE											
-1.965	2.240	-2.363	1.211696	-.028545	1.049373	1.262556	.439240	0.0000000	0.0000000	0.0000000	0.0000000
-1.965	-2.240	2.363	1.126816	.246938	.640449	.727218	-2.141311	.3806641	.3625742	.9524778	.4886889
-1.965	2.363	2.240	1.096247	.820815	.569874	.038804	1.144712	.0080709	-.0235470	-2.9178323	-1.0023381
-1.965	2.363	-2.240	1.126816	.939944	-.339609	.034212	-2.141311	-.7341933	-.0090450	.0123196	.4886889
SOLVING FOR A,B,C,AND K FAILED TO CONVERGE											
-1.965	-2.363	2.240	1.211696	.131730	1.148907	-.743985	*****	0.0000000	0.0000000	0.0000000	0.0000000
2.240	1.965	2.363	1.126816	.246938	.640449	-.727218	-2.141311	.3806641	-.3625742	-.9524778	.4886889
2.240	2.363	1.965	1.126816	.212726	.688833	-.693006	-2.141311	.3535292	-.3716191	-1.0511697	.4886889
-2.240	1.965	2.363	1.096247	.832771	.552966	-.026848	1.144712	.0312855	.0158085	.5052988	-1.0023381
SOLVING FOR A,B,C,AND K FAILED TO CONVERGE											
-2.240	1.965	-2.363	1.211696	5.412507	-1.650031	-.352931	1.654400	0.0000000	0.0000000	0.0000000	0.0000000
-2.240	-1.965	2.363	1.015051	.746676	.040153	-.663975	1.583424	2.8961151	1.4704265	.5077238	-7.3568348
-2.240	2.363	1.965	1.096247	.793968	.607843	.011956	1.144712	-.0393556	-.0077385	.1966302	-1.0023381
-2.240	2.363	-1.965	1.015051	.069743	.997481	.012957	1.583424	-3.6536973	-.7128443	.1951022	-7.3568348
SOLVING FOR A,B,C,AND K FAILED TO CONVERGE											
-2.240	-2.363	1.965	1.211696	.025975	-.169094	1.295863	*****	0.0000000	0.0000000	0.0000000	0.0000000
SOLVING FOR A,B,C,AND K FAILED TO CONVERGE											
2.363	1.965	2.240	1.211696	.394143	-.107322	.992222	.355764	0.0000000	0.0000000	0.0000000	0.0000000
SOLVING FOR A,B,C,AND K FAILED TO CONVERGE											
2.363	2.240	1.965	1.211696	1.114509	-.900211	1.332958	.290791	0.0000000	0.0000000	0.0000000	0.0000000
-2.363	1.965	2.240	1.096247	.820815	.569874	-.038804	1.144712	.0080709	.0235470	2.9178323	-1.0023381
-2.363	1.965	-2.240	1.126816	.939944	-.339609	-.034212	-2.141311	-.7341933	.0090450	-.0123196	.4886889
-2.363	-1.965	2.240	1.015051	.733718	.058478	-.676933	1.583424	.7575822	2.1832708	2.8818930	-7.3568348
-2.363	2.240	1.965	1.096247	.793968	.607843	-.011956	1.144712	-.0393556	.0077385	-.1966302	-1.0023381
-2.363	2.240	-1.965	1.015051	.069743	.997481	-.012957	1.583424	-3.6536973	.7128443	-.1951022	-7.3568348
-2.363	-2.240	1.965	1.126816	.212726	.688833	.693006	-2.141311	.3535292	.3716191	1.0511697	.4886889

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 relaxation 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 LCW .

The calculation of the polycrystalline EPR spectrum is straightforward but complex. The computation may be accomplished 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 magnetic field \bar{H} along the z axis and have the fluctuating microwave field $\bar{H}_1 \cos \omega t$ acting as a perturbation along the x axis. Then in terms of a spin Hamiltonian, the interaction is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = \bar{H} \cdot \tilde{g} \cdot \bar{S} + \bar{H}_1 \cdot \cos \omega t \cdot \tilde{g} \cdot \bar{S} \quad (74)$$

for an $S = 1/2$ system, and ignoring hyperfine interactions.

This Hamiltonian will operate on a basis of $|s, m_s\rangle = |1/2, 1/2\rangle$ and $|1/2, -1/2\rangle$.

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

$$\tilde{g} = \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} \quad (75)$$

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

$$\tilde{R}(\psi, \theta, \phi) = \tilde{R}(\psi) \tilde{R}(\theta) \tilde{R}(\phi) \quad (76)$$

where ψ is a screw rotation around the z axis, θ is the polar angle, and ϕ is the azimuthal angle and

$$\tilde{R}(\psi) = \begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (77)$$

$$\tilde{R}(\theta) = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \quad (78)$$

$$\tilde{R}(\phi) = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (79)$$

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

$$\vec{H} = \begin{pmatrix} 0 \\ 0 \\ H_z \end{pmatrix} \quad (80)$$

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

$$\mathcal{H}_0 = H_z \tilde{R} g \tilde{R}^T \cdot \hat{S} \quad (81)$$

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

$$\Delta E = g_{\text{eff}}^2 \cdot \beta \cdot H_{\text{eff}} \quad (82)$$

where

$$g_{\text{eff}}^2 = g_x^2 \sin^2 \theta \cos^2 \phi + g_y^2 \sin^2 \theta \sin^2 \phi + g_z^2 \cos^2 \theta \quad (83)$$

and

$$H_{\text{eff}} = \hbar \omega / g_{\text{eff}} \cdot \beta \quad (84)$$

where ω is the microwave frequency and β is the Bohr magneton and is independent of ψ .

If we represent the eigenvector of this operator as

$$|\psi^\pm\rangle = a_\pm | +1/2 \rangle + b_\pm | -1/2 \rangle \quad (85)$$

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

$$I = |\langle \psi^+ | \frac{1}{H_1} | \psi^- \rangle|^2 \quad (86)$$

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 θ' and ϕ' . The intensity of an arbitrary orientation specified by θ' and ϕ' 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_{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 θ, ϕ . 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 $\text{Fe}(\text{TPP})(\text{S}\phi)(\text{HS}\phi)$. 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

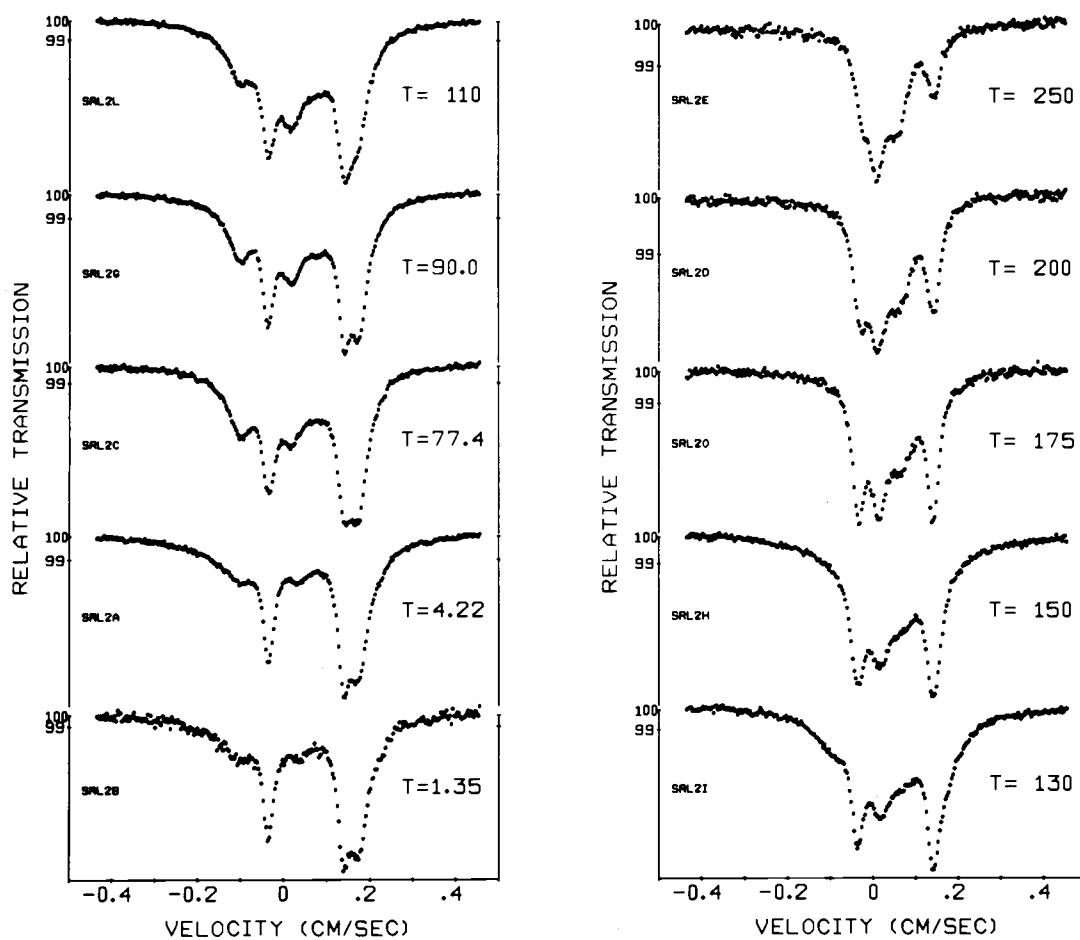


Figure 5. Mossbauer spectra of $\text{Fe(TPP)(S}\phi\text{)(HS}\phi\text{)}$ as a function of temperature (temperature in K). Material from T. Sorrell.

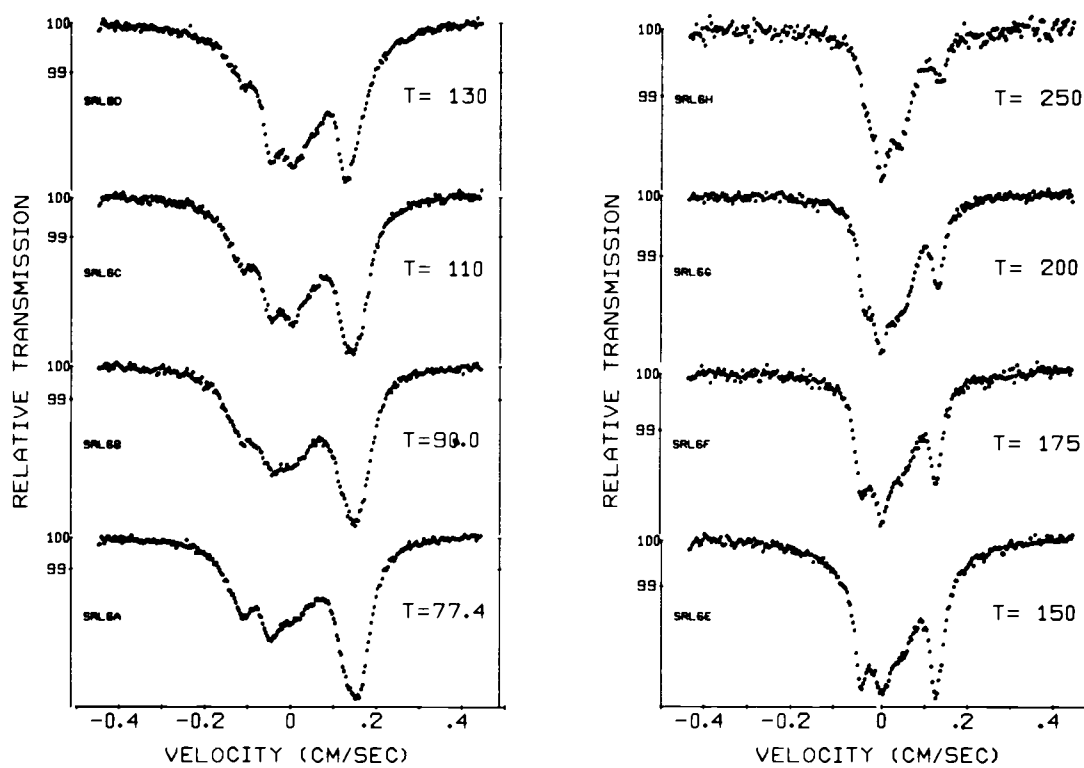


Figure 6. Temperature dependent Mossbauer spectra of $\text{Fe(TPP)(S}\phi\text{)(HS}\phi\text{)}$. Sample from T. Sorrell.

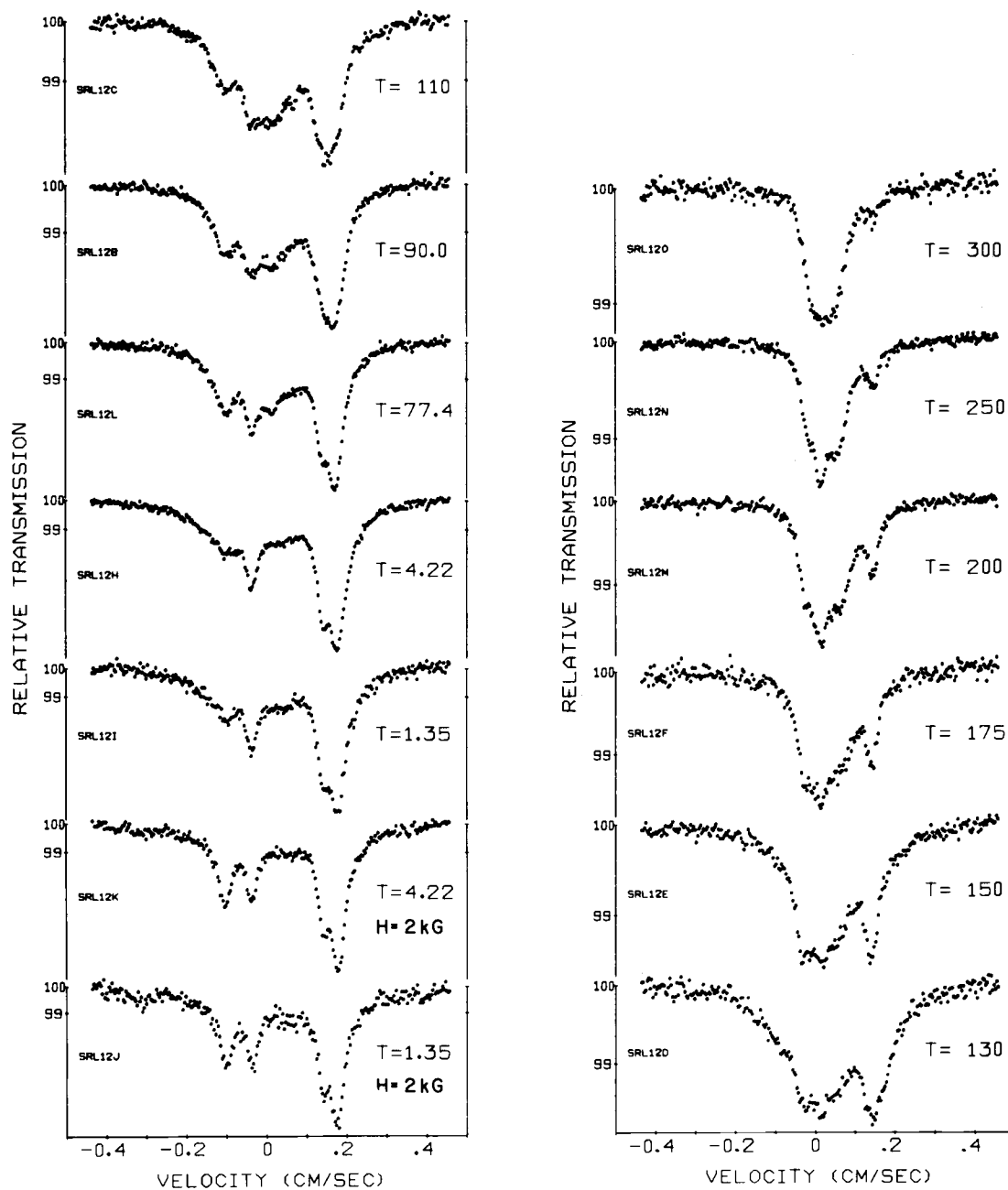


Figure 7. Temperature dependent Mossbauer spectra of $\text{Fe}(\text{TPP})(\text{S}\phi)(\text{HS}\phi)$. Sample from W.E. Silverthorn.

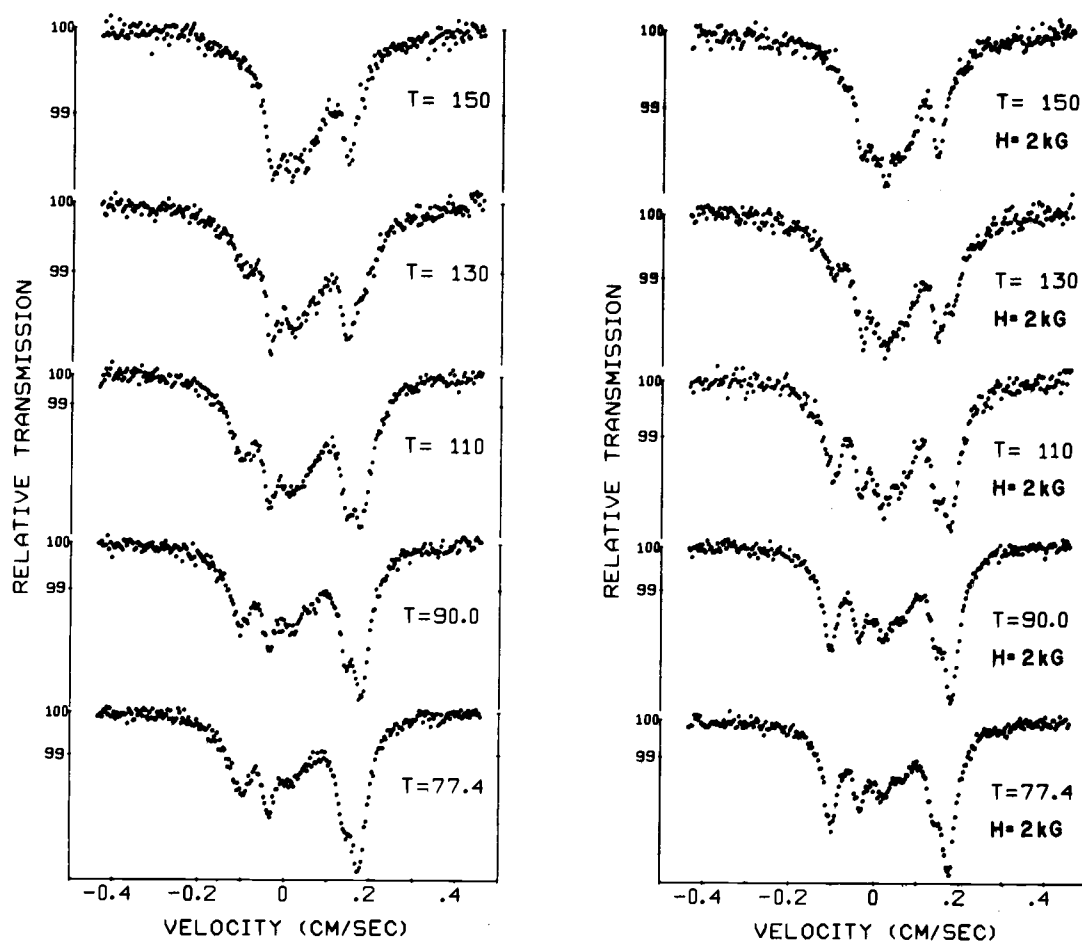


Figure 8. Temperature dependent Mossbauer spectra of SRL 14 both in and out of a magnetic field.

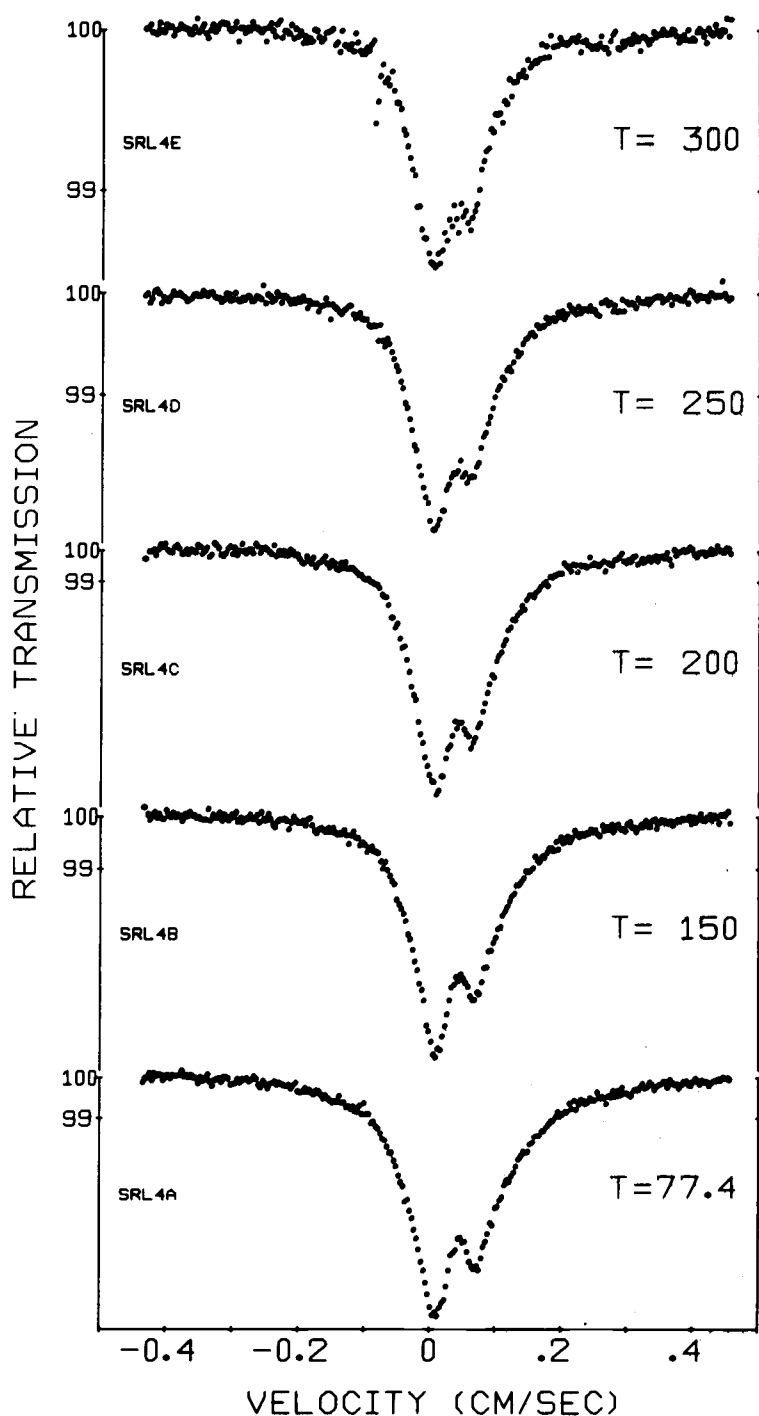


Figure 9. Temperature dependent Mossbauer spectra of SRL 2 allowed to decompose on air. Spectra are typical of high-spin ferric porphyrin.

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 431.4×10^{-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.

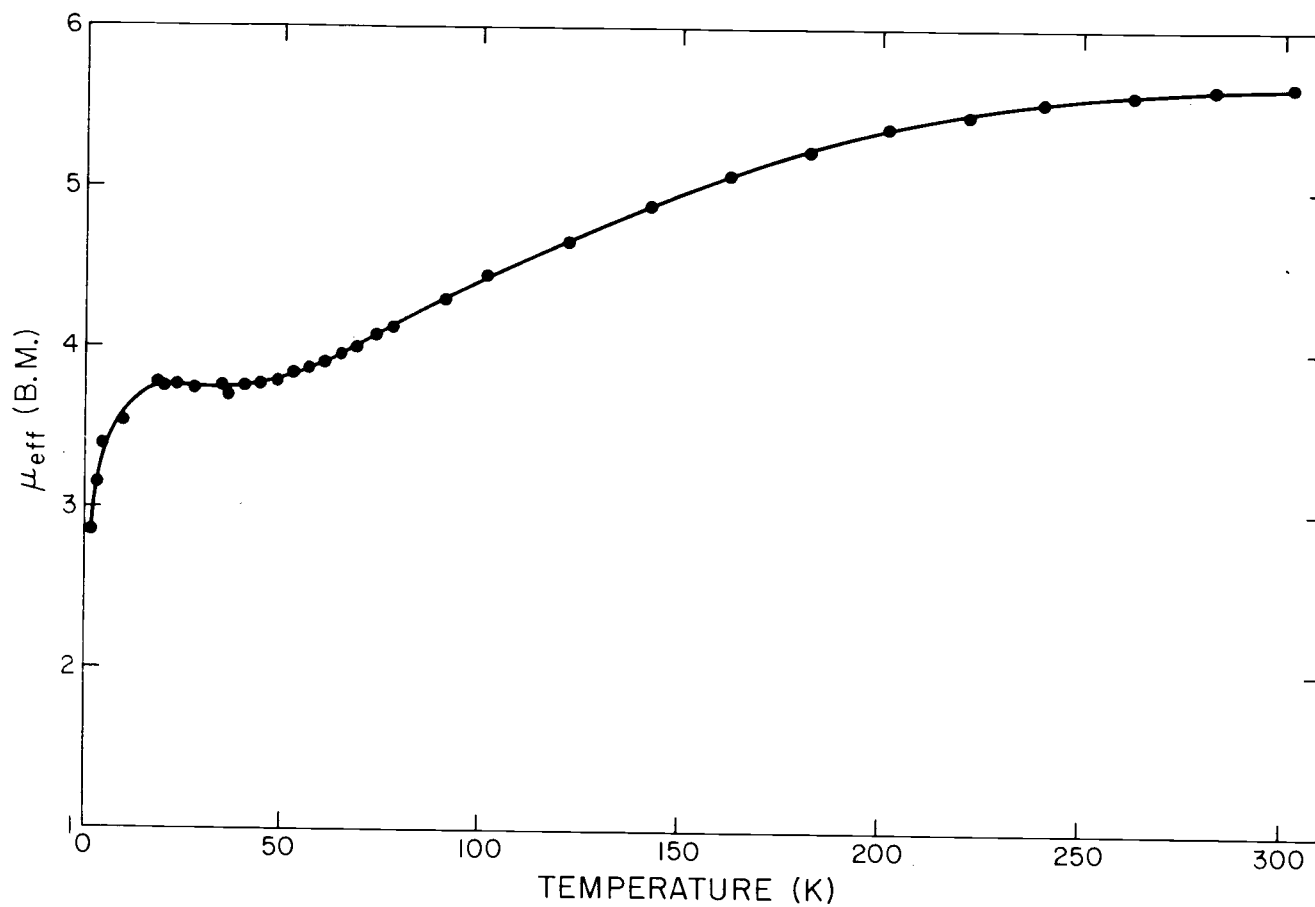


Figure 10. Effective magnetic moment of SRL12 as a function of temperature.

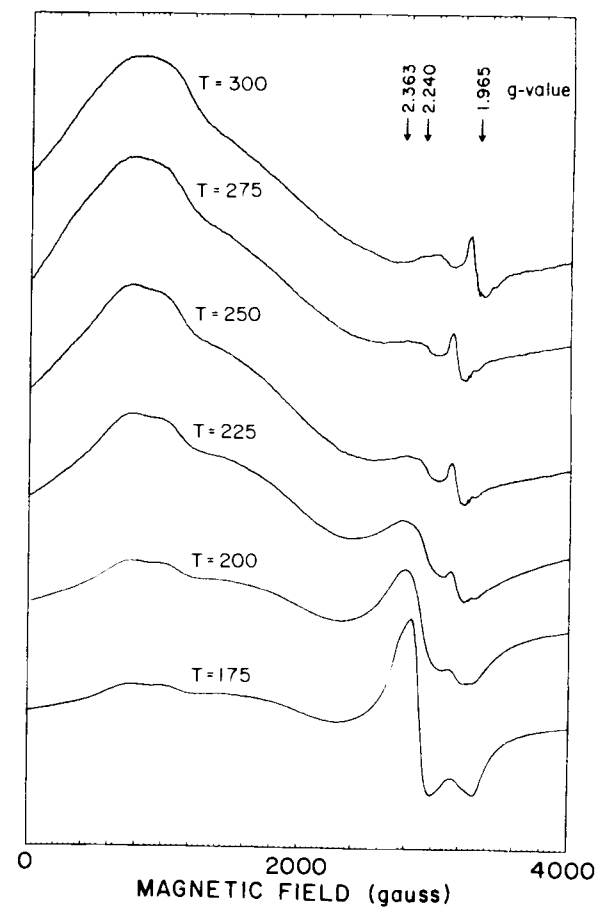
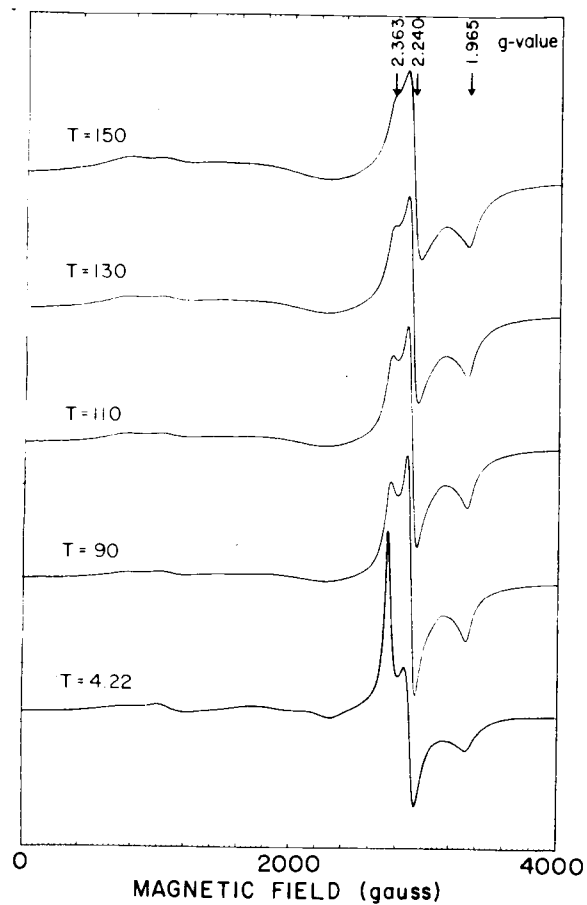


Figure 11. EPR spectra of SRL12 as a function of temperature. Temperature in K. Microwave frequency for temperature 4.2 to 275 K is 9.145 GHz, at 300 K $\nu = 9.531$ GHz. The g values on the graph are for $\nu = 9.145$ GHz.

VI. DATA ANALYSIS

A. Mossbauer Spectra

The Mossbauer data for $\text{Fe}(\text{TPP})(\text{S}\phi)(\text{HS}\phi)$ 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, ΔE_Q , and isomer shift, δ , 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 4. Mossbauer parameters for the three components RLX, IMP, and HI on Fe(TPP) (S ϕ) (HS ϕ) at selected temperatures.

Temperature			Component			
	RLX		IMP		HI	
			Parameter			
	ΔE_1 (cm/sec)	δ_1 (cm/sec)	ΔE_2 (cm/sec)	δ_2 (cm/sec)	ΔE (cm/sec)	δ (cm/sec)
4.22 K	0.282 \pm 0.003	0.038 \pm 0.003	0.175 \pm 0.003	0.053 \pm 0.003	*	*
77	0.274	0.037	0.172	0.054	0.050 \pm 0.007	0.044 \pm 0.05
130	0.278	0.038	0.178	0.054	0.050	0.038
175	*	*	0.174	0.055	0.053 \pm 0.003	0.040 \pm 0.003
250	*	*	0.169	0.061	0.048	0.034

*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

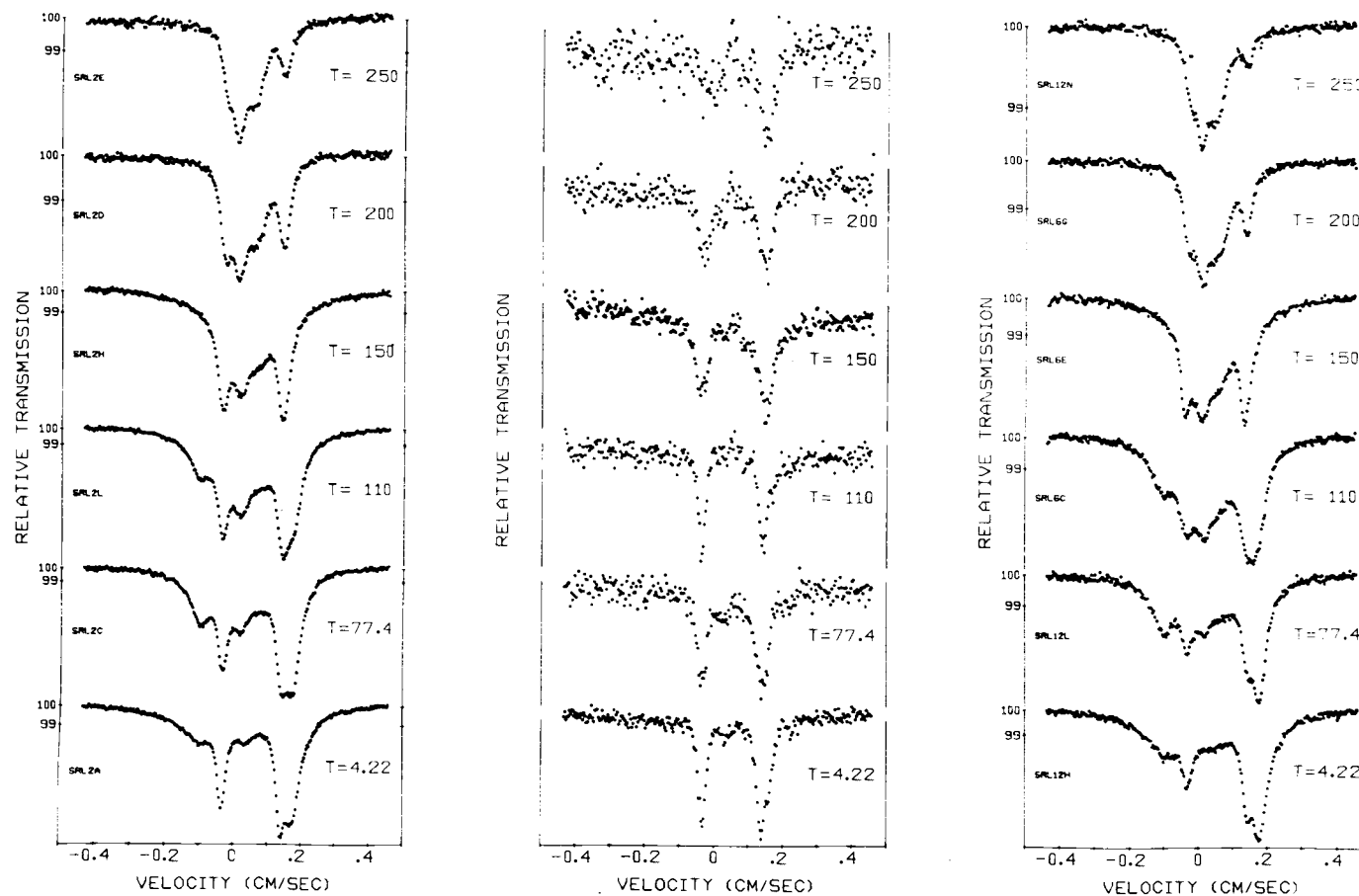


Figure 12. Difference spectrum (center) of selected Mossbauer spectra at the same temperature. Weighting factors used in taking the difference were chosen to minimize the RLX component (4.2 K to 110 K) or minimize the HI component (150 K to 250 K). This shows IMP to be a symmetric quadrupole doublet.

sample yielded identical Mossbauer patterns. Due to the excellent analysis of the material we feel that the presence of two magnetic environments for Fe^{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 show 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.

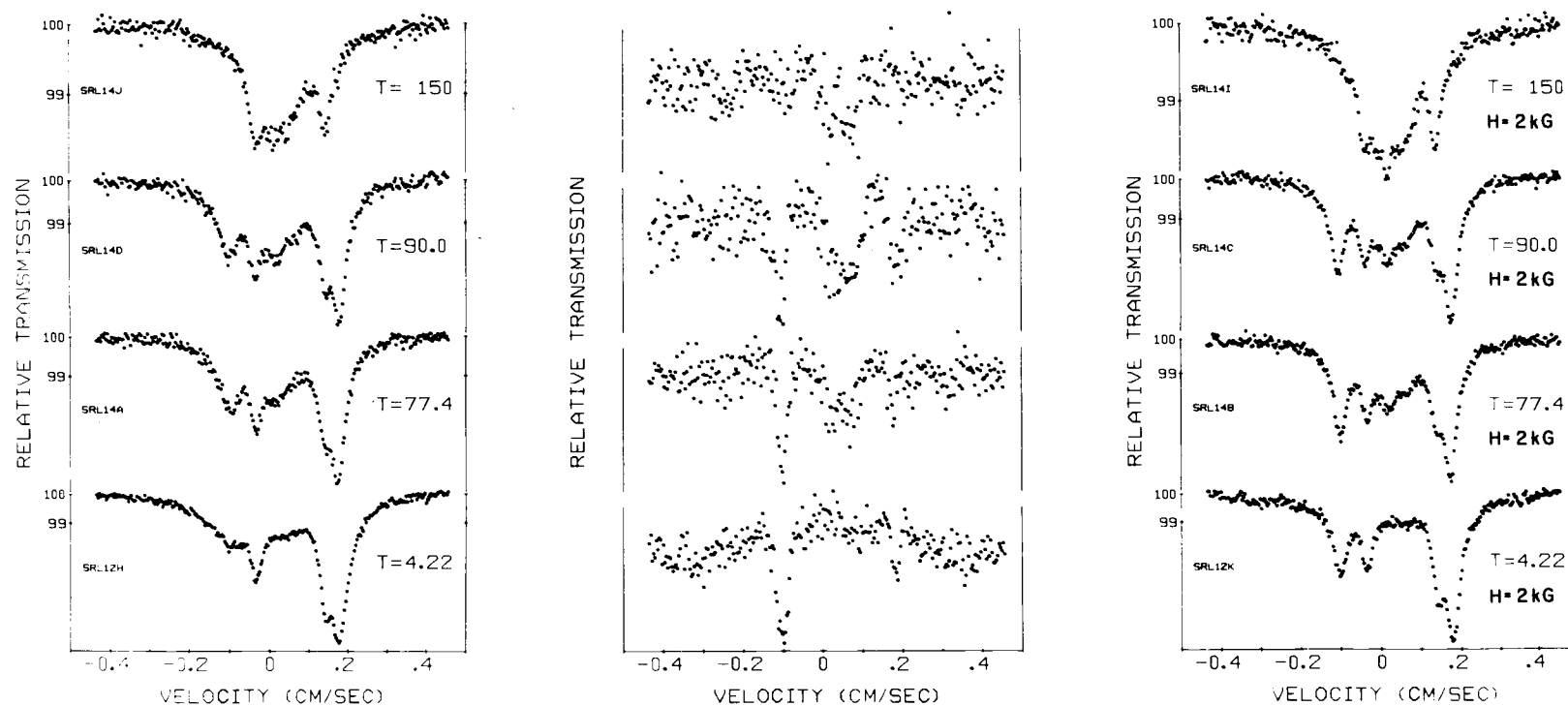


Figure 13. Mossbauer spectra of a sample both in and out of a polarizing magnetic field. Difference spectrum is shown in the middle.

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

($E \neq 0$ 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 $\text{Fe}(\text{TPP})(\text{S}\phi)$ ($\text{HS}\phi$) 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 μ_{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]).

Sample	D/ λ	E/ λ	Crystal Field Parameters				
			E/D	k	g_x	g_y	g_z
P-450	-2.34966	0.52284	-0.22252	1.1463	-2.417	2.249	-1.921
LOW	-3.65370	0.71284	-0.19510	1.58342	-2.363	2.240	-1.965
Coefficients of the Wavefunction					$ \psi^\pm\rangle = A_i \pm 1^\pm\rangle \pm B_i \zeta^\mp\rangle + C \mp 1^\pm\rangle$		
	i	A_i	B_i	C_i	$(E_i - E_1)/\lambda$		
LOW	1	-0.06974	-0.99748	-0.01296	0		
	2	-0.77801	0.06252	0.62513	8.849		
	3	0.62437	-0.03352	0.78041	13.221		
P-450	1	0.1116	0.9935	-0.0229	0		
	2	0.7954	-0.1031	-0.5972	5.533		
	3	0.5957	-0.0484	0.8017	8.778		

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, κ , 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 $\frac{e^2qQ}{4} = 1.5 \times \frac{7}{\langle r^{-3} \rangle} q_{\text{val}}$ mm/sec [53] 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 π 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, $P\kappa/g_n\beta_n$; and the Fermi contact constant, κ . By allowing $P\kappa/g_n\beta_n$ 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 η 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 λ , 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]).

Parameter	P450	LOW
g_x	1.91	-2.363
g_y	2.26	2.240
g_z	2.45	-1.965
$A_{xx}/g_n \beta_n$ (KG)	-450	43
$A_{yy}/g_n \beta_n$ (KG)	102	-71
$A_{zz}/g_n \beta_n$ (KG)	191	340
N_{xy}^2	0.96	0.95 ± 0.05
N_{xz}^2	0.80	0.80 ± 0.1
N_{yz}^2	0.80	0.80 ± 0.1
ΔE_Q (cm/sec)	0.285	-2.282
η	-1.80	0.0
$eQV_{zz}/4$ (cm/sec)	0.099	-0.141
δ (cm/sec)	0.038	0.038
Γ (linewidth in cm/sec)	0.030	0.030
VJ2 (MH _z)	--	45 ± 5
κ	1.14	0.625 ± 0.025

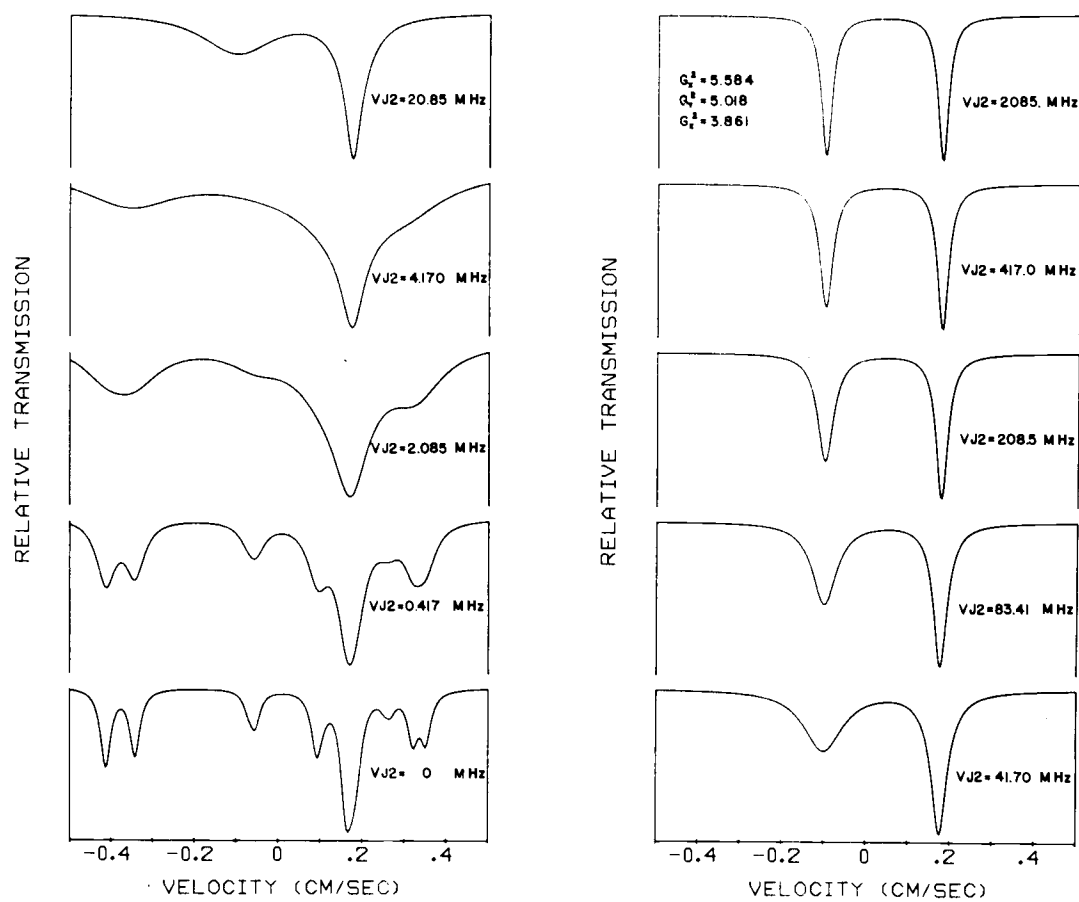


Figure 15. RLX using parameters from Table 6 as a function of the relaxation rate constant $VJ2$.

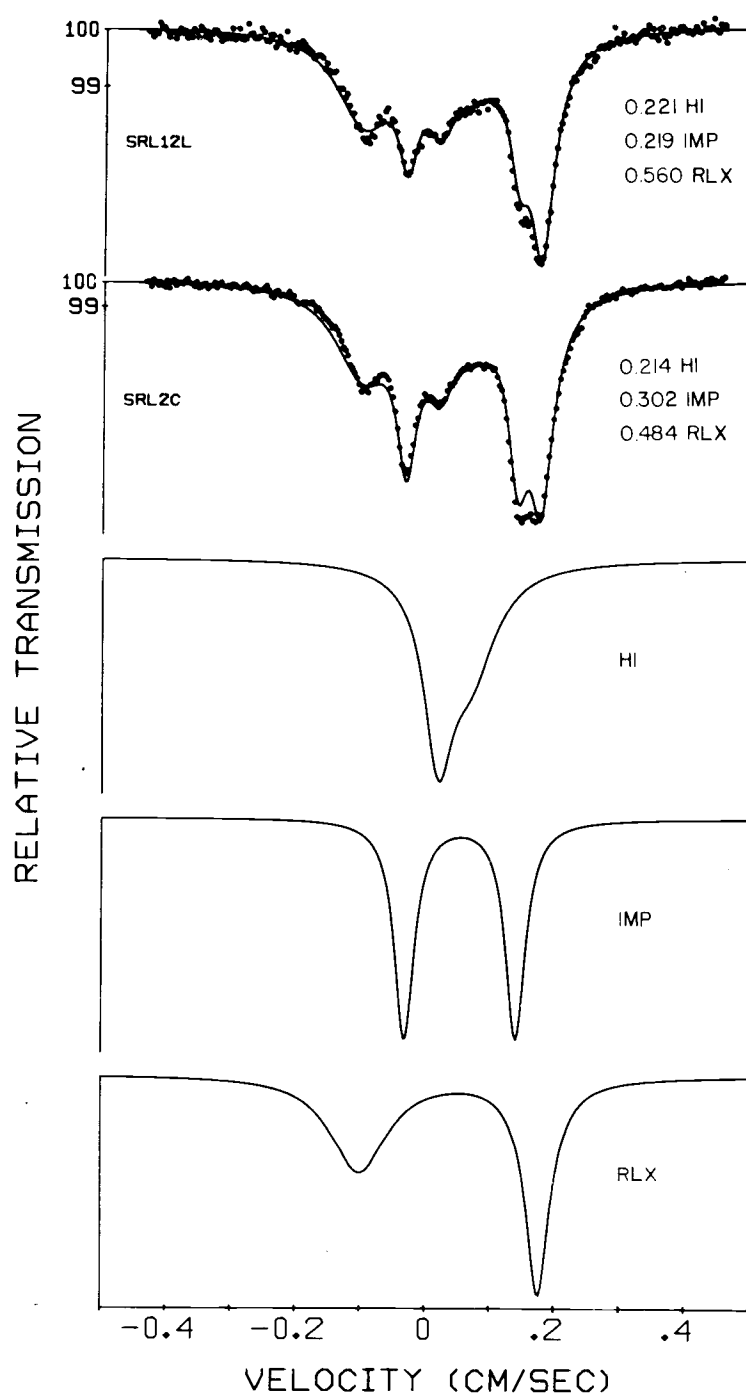


Figure 16. The three components which are summed to simulate the spectra of $\text{Fe}(\text{TPP})(\text{HS}\phi)(\text{S}\phi)$. Parameters for HI and IMP from Table 4. Parameters for RLX from Table 6.

η and $e^2 q Q / 4$ 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 $\text{Fe}(\text{TPP})(\text{S}\phi)(\text{HS}\phi)$, 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 sub-routines from locally available libraries were used in these programs and are listed below.

COMLOT 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 SWMPLOT

OS3 FORTRAN VERSION 3.13

02/12/76 1559

```

PROGRAM MOSSRED
C REVISION NO. 4, 21 JULY 1976
C THIS PROGRAM NORMALIZES AND PLOTS NO-2400 RAW DATA. THE LATTER
C HAS PREVIOUSLY BEEN READ FROM PAPER TAPE AND STORED ON DISC FILES
C LABELED BY THE EXPERIMENTAL DESCRIPTOR (EG. DTG49). UP/DOWN
C MULTISCALING IS ASSUMED SO NO FOLDING OPTIONS EXIST.
C LOGICAL UNITS USED BY MOSSRED.
C
C     LUN 10 = PLOTTER
C     LUN 15 = LINE PRINTER
C     LUN 16 = PUNCH
C
C THESE LUNS MUST BE EXTERNALLY EQUIPED AND LABELED BEFORE
C RUNNING THE PROGRAM:
C
C     LUN 20 = DATA
C
C THIS FILE IS INTERNALLY EQUIPED BY THE PROGRAM AND THEREFORE
C MUST BE FREE.
C
C THE FOLLOWING SYMBOLS ARE THE INPUT PARAMETERS TO THE PROGRAM.
C
C     N=NUMBER OF INITIAL POINTS TO BE READ. IF N IS GREATER
C     THAN 1200, THE PROGRAM ENDS.
C     IF N = 0, THE PROGRAM USES THE OPTION TO GENERATE A PLOT
C     (ONLY) FROM OUTPUT CREATED BY THIS PROGRAM, AND READS
C     THE DECKS PRODUCED.
C     ND=NUMBER OF INITIAL POINTS TO BE DELETED.
C     NDLY=NUMBER OF DELAY PULSES.
C     OVF=NUMBER OF OVERFLOWS.
C     CG=CENTROID OF SPECTRUM.
C     VELC=CALIBRATION CONSTANT IN MM/SEC/CH.
C     NOPT=OPTIONAL PLOT FLAG. IF NOPT IS NON-ZERO THE
C     OPTIONAL PLOT IS GENERATED. IF NOPT IS ZERO
C     THE OPTIONAL PLOT IS NOT GENERATED.
C     TEXT=AN ARRAY OF DIMENSION 9 WHICH IS THE TITLE FOR THE PLOT.
C     TEXT(1) MUST CONTAIN THE EXPERIMENTAL DESCRIPTOR LEFT
C     JUSTIFIED.
C     FLAG=OPTIONAL FLAG. IF FLAG IS ONE THE BACKGROUND OF MOSSBAUER
C     SPECTRA IS CORRECTED FOR SLOPE BY PATIO METHOD.
C     *****NOTE: FLAG IS AN INTEGER VALUE (IMPORTANT)*****
C
C IF CG AND VELC ARE NON-ZERO THE PLOT WILL CONTAIN AN ABCISSA
C IN CHANNEL UNITS AND AN ADDITIONAL ABCISSA IN UNITS OF MM/SEC.
C
C INPUT:
C
C TO RUN THE PROGRAM, THE FILE(S) TO BE USED MUST EXIST AND
C HAVE BEEN EDITED AND STORED UNDER THE NAME OF THE EXPERIMENTAL
C DESCRIPTOR. ALL TITLES, COMMENTS, AND EXTRA CHANNEL COUNTERS MUST
C HAVE BEEN REMOVED FROM THE FILE, SINCE THE PROGRAM READS ONLY
C THE DATA FROM THIS FILE.
C IF A REPLOT OF ANY NORMALIZED SPECTRA IS DESIRED, THE ABOVE INSTRUCTIONS ARE
C NOT USED. THE METHOD USED TO REPLOT SUCH DATA DEPENDS ON WHETHER AN
C AUTOSCALING CARD EXISTS WITH THE DATA: WITH AUTOSCALING CARD THE VALUES OF
C CG, VELC, AND AN ADDITIONAL VELOCITY AXIS ARE PRESENT. WITHOUT AUTOSCALING
C CARD THE USER MUST CREATE AN AUTOSCALING CARD WITH THE FOLLOWING VALUES
C YMAX=9., YMIN=0., CG=0., VELC=0., NTOT, AND NZERO. THE VALUES OF CG, VELC,
C AND ADDITIONAL VELOCITY AXIS ARE NOT PRESENT. THIS METHOD WILL PRODUCE AN
C AUTO SCALING CARD AND A LABEL CARD.

```

OS3 FORTRAN VERSION 3.13

02/12/73 1659

C THE VALUES OF YMAX, NTOT, AND NZERO ARE ABSOLUTELY NECESSARY FOR THE
C DETERMINATION OF THE Y-AXIS IN THE PLOT. YMAX IS REQUIRED TO EQUAL ZERO
C (YMAX=0.), IN ORDER FOR THE NEW AUTOSCALING CARD TO BE PUNCHED.

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

C CARD 1: N, ND, NDLY, OVF, CG, VELC, NOPT, FLAG
C (3I5, 3F10.5, 2I5)

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

C THE ABOVE IS CARD SET 1

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

C CARD 3: (BLANK CARD)

C CARD 4: TITLE CARD (SAME AS CARD 2)

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

C * NORMALIZED DATA DECK *

C THE ABOVE IS CARD SET 2.

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

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

C CARD 3

C CARD 4

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

C * NORMALIZED DATA DECK *

C THE ABOVE IS CARD SET 3.

C ADDITIONAL ARRAYS AND PARAMETERS USED

C IDAT(1200)=ARRAY OF INITIAL RAW DATA.

C RDAT(1200)=ARRAY OF NORMALIZED DATA.

C ARRAY(9)=ARRAY USED TO TRANSMIT LABELS FOR PLOTS.

C NZERO=ND+NDLY, THE NUMBER OF POINTS AT THE BEGINNING
C WHICH ARE SET TO ZERO.

C ADD=OVF*1048576, THE NUMBER OF COUNTS TO BE ADDED TO
C THE RAW DATA FOR OVERFLOWS.

C FACT=NORMALIZING FACTOR OBTAINED BY AVERAGING 5 POINTS
C AT EACH OF THE OUTER EXTREMES OF THE SPECTRA AND
C SETTING THAT TO 100.

C YMAX=LARGEST VALUE OF RDAT.

C YMIN=SMALLEST VALUE OF RDAT.

C OUTPUT: THE FOLLOWING IS CONTAINED ON THE OUTPUT UNITS.

C PUNCH:

C 1) LABEL CARD WITH TEXT(1) AS A LABEL.

C 2) TITLE CARD WITH TEXT(I) ON IT.

C 3) PARAMETER AND AUTOSCALING CARD CONTAINING
C YMAX, YMIN, CG, VELC, NTOT, NZERO, FLAG
C (3F10.5, F10.8, 3I5)

C 4) THE NORMALIZED DATA AND CORRESPONDING CHANNEL NUMBER.

OS3 FORTRAN VERSION 3.13

02/12/78 1659

C (I,RDAT(I),I=1,NTOT)
C (6(I4,F8.4))
C

LINEPRINTER:

- 1)TEXT(I) AT TOP OF PAGE AS TITLE.
- 2)CONSTANTS OF CALCULATION
(N, ND, NOLY, OVF, 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 (YMAX, YMIN, NTOT, NZERO, FLAG)
- 6)NORMALIZED DATA (I,RDAT(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 ORDINATE 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 ORDINATE OF 7.57 INCHES
AND AN ABCISSA OF 8.95 INCHES.

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

C FROM TELETYPE (DECKNAME OF MOSSRED IS ASSUMED)

C >FORTRAN,I=MOSSRED,O,E,X

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

C >SAVE,56=MOSSREDB

C TO CREATE A PUNCHED DECK, USE: (UNLESS OTHERWISE EQUIPPED.
C LUN 62=PUN)

C >LABEL,62/SMITH (OR WHATEVER NAME YOU WANT)

C >COPY,I=MOSSREDB,O=62

C TO RUN THE DECK JUST CREATED, FROM BATCH, USE THE FOLLOWING DECK:

C >JOB,.....

C >EQUIP,10=PLOT

C >EQUIP,15=LP

C >EQUIP,16=PUN

C >LABEL,10/SAVE FOR SMITH

C >LABEL,15/SAVE FOR SMITH

C >LABEL,16/SMITH

(LIMIT OF 7 CHARACTERS ON PUNCH LABEL)

C >FORMS,10/PT-05 PLEASE

(MOUNT FINE RAPIDOGRAPH PEN ON PLOTTER)

C >TIME = 200

(GIVES ENOUGH TIME TO RUN)

C >MF3LKS = 400

(GIVES YOU ENOUGH FILE SPACE FOR RUN

EACH SPECTRA REQUIRES ABOUT 40 FILE

OS3 FORTRAN VERSION 3.13

02/12/78 1659

```

C                                BLOCKS. THE LIMITS OF YOUR JOB
C                                NUMBER SHOULD BE CHECKED FOR THIS.)
C
C      ≥LOAD,L=*COMLOT,L=*KEITHL3 (LOAD BINARY AND SATISFY PLCTTING
C                                EXTERNALS FROM *COMLOT, AND LABELP
C                                FROM *KEITHL3.)
C
C      <BINARY DECK>
C      ≥≥
C      RUN
C      (SUGGESTED ORDER OF CARD SETS)
C      (ANY PERMUTATION OF THESE CARD SETS MAY EXIST IN ANY ORDER)
C      SET 1
C      .
C      .
C      .
C      SET 1
C      SET 2
C      .
C      .
C      .
C      SET 2
C      SET 3
C      .
C      .
C      .
C      SET 3
C      CARD 1 WITH N>1200
C      ≥LOGOFF
C
C      END OF INSTRUCTION FOR PROGRAM MOSSRED.
C
C      PROGRAM FOLLOWS AFTER THE LINE OF **S.
C
C      *****
C
C
C
C      DIMENSION IDAT(1200), ROAT(1200), TEXT(9), ARRAY(9)
C      DIMENSION CUTOUT(3)
C      DIMENSION BCKGRN(4)
C      DATA (CUTOUT= 20HCUT ALONG SOLID LINE)
C      DATA (BCKGRN= 25H BACKGROUND CORRECTED)
C      INTEGER FLAG
C
C      READ IN INITIAL PARAMETERS AND TEST EXIT CRITERIA (N>1200)
C
C 90      READ 100, N,ND,NDLY,OVF,CG,VELC,NOPT,FLAG
C 100     FORMAT (3I5,3F10.5,2I5)
C         IF (N.GT.1200) CALL EXIT
C         IF (N.EQ.0) GO TO 350
C         READ 110, (TEXT(I),I=1,9)
C 110     FORMAT (9A3)
C
C      LABEL PUNCH WITH TEXT(1) AND WRITEOUT TEXT ON PUNCH AND LP.
C
C      CALL LABELP (16,TEXT(1))
C      CALL EQUIP (20,TEXT)
C      WRITE (15,130) (TEXT(I),I=1,9)
C      WRITE (16,135) (TEXT(I),I=1,9)

```

OS3 FORTRAN VERSION 3.13 MOSSRED 02/12/78 1659

```

130  FORMAT (1H1,9A8)
135  FORMAT (9A8)
C
C  READ IN IDAT ARRAY.
C
      READ(20,120) (IDAT(I),I=1,N)
120  FORMAT (9(I6,1X),I6)
C
C  WRITE OUT CONSTANTS OF CALCULATION AND HEADINGS ON LINE PRINTER.
C
      WRITE (15,140) N,ND,NOLY,OVF,CG,VELC,TEXT(1)
140  FORMAT (1H-,5X,*,CONSTANTS OF CALCULATION*,//,
1      5X,*,NUMBER OF DATA POINTS      N =*,I5,/,
2      5X,*,NUMBER OF POINTS DELETED ND =*,I5,/,
3      5X,*,NUMBER OF POINTS DELAY      NDL =*,I5,/,
4      5X,*,NUMBER OF OVERFLOWS        OVF =*,F5.0,/,
5      5X,*,CENTROID IN CHANNELS        CG =*,F10.5,/,
6      5X,*,CAL CONST (MM/SEC/CH)      VELC =*,F10.8,/,
7      5X,*,INPUT DATA IS FROM FILE *,A8)
C
C  CHECK FOR BACKGROUND SLOPE FLAG.
C
      IF (FLAG.NE.1) GOTO 145
      WRITE (15,146)
146  FORMAT (5X,*,BACKGROUND SLOPE CORRECTED*)
C
145  WRITE (15,150)
150  FORMAT (1H0,26X,*,EXPERIMENTAL RESULTS*)
      WRITE (15,160)
160  FORMAT (1H0,1X,6(*CHA  COUNT *),/)
C
C  ADD OVERFLOWS AND PRINT OUT EXPERIMENTAL RESULTS
C
      NZERO=ND+NOLY
      NTOT=N+NOLY
      NOLY1=NOLY+1
      ND1=NC+1
      NZERO1=NZERO+1
      ADD=OVF*1048576.0
      DO 170 I=ND1,N
      K=I+NOLY
170  RDAT(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 (1X,6(I4,F8.0))
C
C  DETERMINES NORMALIZING FACTOR.
C
      AVG1=AVG2=0.0
      N1=NZERO+3
      N2=NZERO+7
      N3=NTOT-7
      N4=NTOT-3
      DO 200 K=N1,N2
200  AVG1=AVG1+RDAT(K)
      DO 210 K=N3,N4
210  AVG2=AVG2+RDAT(K)
C
C  CHECK FOR CORRECTION OF BACKGROUND SLOPE FLAG.

```

OS3 FORTRAN VERSION 3.13 MOSSRED 02/12/78 1659

```

C
  IF (FLAG.NE.1) GOTO 215
  CALL BKGCOR(RDAT,NTOT,AVG1,AVG2,NZERO1)
C
C
C NORMALIZATION OF SPECTRUM.
C
C DETERMINATION OF YMAX AND YMIN.
C
215  YMIN=100.
     YMAX=100.
     FACT=1000./ (AVG1+AVG2)
     DO 220 I=NZERO1,NTOT
     RDAT(I)=RDAT(I)*FACT
     IF (RDAT(I) .GT. YMAX) YMAX=RDAT(I)
220  IF (RDAT(I) .LT. YMIN) YMIN=RDAT(I)
C
C PRINT HEADINGS AND SCALING FACTORS ON LP.
C
     WRITE (15,130) (TEXT(I),I=1,9)
     WRITE (15,248) YMAX,YMIN,NTOT,NZEFO
     WRITE (15,230)
230  FORMAT (1H0,26X,#NORMALIZED SPECTRUM#)
C
C CHECK BACKGROUND SLOPE FLAG.
C
     IF (FLAG.NE.1) GOTO 235
     WRITE (15,236)
236  FORMAT (1H0,26X,#BACKGROUND SLOPE CORRECTED#)
C
235  WRITE (15,240)
240  FORMAT (1H0,1X,6 (#CHA  INTEN #),/)
C
C PUNCH OUT PARAMETER CARD WITH AUTOSCALING INFORMATION.
C
     WRITE (16,245) YMAX,YMIN,CG,VELC,NTOT,NZERO,FLAG
245  FORMAT (3F10.5,F10.8,3I5)
248  FORMAT (/5X,#INTENSITY MAX = #,F10.5,5X,#INTENSITY MIN = #
1,F10.5,5X,#NO. OF POINTS = #,I4,5X,#NO. OF LEADING ZEROS = #
2,I4,/)
C
C PRINT AND PUNCH NORMALIZED SPECTRUM.
C
     WRITE (15,251) (I,RDAT(I),I=1,NTOT)
     WRITE (16,250) (I,RDAT(I),I=1,NTOT)
250  FORMAT (6(I4,F8.4))
251  FORMAT (1X,6(I4,F8.3))
     GO TO 860
C
C THIS OPTION (IF N=0) ALLOWS THE USER TO RE-PLOT A SPECTRA, READING
C THE DECK FROM CARDS GENERATED BY THIS PROGRAM
C
850  READ 135,(TEXT(I),I=1,9)
     READ 245,YMAX,YMIN,CG,VELC,NTOT,NZERO,FLAG
     READ 250,(J,RDAT(I),I=1,NTOT)
     NZERO1 = NZERO + 1
860  CONTINUE
C
C IF AUTOSCALING CARD IS NOT PRESENT THIS OPTION WILL PUNCH ONE.
C

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OS3 FORTRAN VERSION 3.13 MOSSRED 02/12/78 1659

```

      IF (YMAX.NE.0.) GO TO 866
      YMAX = YMIN = 100.
      DO 865 I=NZERO,NTOT
      IF (RDAT(I).GT.YMAX) YMAX = RDAT(I)
865  IF (RDAT(I).LT.YMIN) YMIN = RDAT(I)
      WRITE(16,245) YMAX,YMIN,CG,VELC,NTOT,NZERO,FLAG
      CALL LABELP (16,TEXT(1))
C
C  BEGIN PLOTTING SEQUENCE.
C  PLOT INTENSITY VS CHANNEL NUMBER
C
866  CALL VECTORS
C
C  DRAW BOX AROUND PLOT FOR CUTTING PURPOSES.
C
      CALL SIZE (27.,10.)
      CALL SCALE (1.,1.,0.,0.,0.,0.)
      CALL PLOT (0.,0.,0,0)
      CALL PLOT (11.,0.,1,0)
      CALL PLOT (11.,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 (5.50,8.2,1,28)
      CALL PLOT (9.75,8.2,1,28)
      CALL SYMBOL (4.3,8.55,0,...12,20,CUTOUT)
      CALL VECTORS
C
C  SET UP SCALING OF PLOT
C
      XMAX=NTOT
      XMIN=NZERO1
      XDIF=XMAX-XMIN
      YDIF=YMAX-YMIN
      YMIN=YMIN-(.50*YDIF)
      YMAX=YMAX+(.50*YDIF)
      YDIF=YDIF*2.0
C
C  DEFINE PHYSICAL BOUNDRIES
C
      XSCAL=8.5455/XDIF
      YSCAL=6.5636/YDIF
      CALL SCALE (XSCAL,YSCAL,1.5,1.,XMIN,YMIN)
C
C  DISPLACEMENT FOR DRAWING CAPTIONS
C
      XXDIS=.24/XSCAL
      XYDIS=.64/XSCAL
      YXDIS=.24/YSCAL
      YYDIS=.08/YSCAL
C
C  DRAW AND LABEL X-AXIS
C
      ENCODE (3,310,ARRAY) XMIN
310  FORMAT(F3.0)
      CALL SYMBOL (XMIN-XXDIS,YMIN-YXDIS,0,...16,3,ARRAY)
      CALL PLOT (XMIN,YMIN,0,0)
      CALL PLOT (XMIN,YMIN,1,8)
      XP=IXF=NZERO1/10

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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-XXDIS,YMIN-YXDIS,0...16,3,ARRAY)
      CALL PLOT (XMIN,YMIN,0,0)

C
C  DRAW Y-AXIS
C
      YP=IYF=YMIN
      IPP=YMIN+.5
      YLMK=YP+.1
      YHMK=IHP=YMAX
      YP=YP+.5
      IF (IYP.NE.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.LT.YHMK) GO TO 340
      IF (YP.GE.YMAX) GO TO 360
      CALL PLOT (XMIN,YP,1,5)
360  CALL PLOT (XMIN,YMAX,1,0)

C
C  LABEL Y-AXIS
C
      ENCODE (3,310,ARRAY) YLMK
      CALL SYMBOL (XMIN-XYDIS,YLMK-YYDIS,0...16,3,ARRAY)
      ENCODE (3,310,ARRAY) YHMK
      CALL SYMBOL (XMIN-XYDIS,YHMK-YYDIS,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...12,25,3CKGRN)

C
365  CALL POINTS
C
C  PLOT DATA
C
      DO 370 I=NZERO1,NTOT
      FI=I
370  CALL PLOT (FI,ROAT(I),1,27)

      CALL VECTORS
      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
700  FORMAT (4X,*,CAL CONST = *,F10.7,*,MM/SEC/CH*,5X,*,CG = *,F10.4,
      I*,CHANNELS*)

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DS3 FORTRAN VERSION 3.13 MOSSRED 02/12/78 1659

```

      CALL SYMBOL (XMIN,YMAX-(.3/YSCAL),0.,.12,65,AFRAY)
C
C THIS CODE GENERATES THE VELOCITY AXIS ON THE DATA PLOT
C IF CG IS NON-ZERO. FOR THIS SECTION, THE FOLLOWING
C PARAMETERS ARE IMPORTANT.
C
C      VELMIN=MINIMUM IN VELOCITY CORRESPONDING TO XMIN.
C      VELMAX=MAXIMUM IN VELOCITY CORRESPONDING TO XMAX.
C      VAX=OFFSET OF VELOCITY AXIS ABOVE CHANNEL AXIS.
C      (.5 INCHES ABOVE)
C      VLMK=LOW VALUE ON VEL AXIS TO BE LABELED.
C      VHMK=HIGH VALUE ON VEL AXIS TO BE LABELED.
C
C SET UP INITIAL PARAMETERS REQUIRED.
C
      VELMIN = (XMIN-CG)*VELC
      VELMAX = (XMAX-CG)*VELC
      VEL1 = 1./VELC
      VLMK = IVL = VELMIN
      DEL = VLMK - VELMIN
      VAX = .5/YSCAL + YMIN
      VHMK = IVH = VELMAX
C
C DRAW VELOCITY AXIS.
C
      CALL PLOT(XMIN,VAX,0,0)
      VPOS = XMIN + DEL/VELC
800   CALL PLOT(VPOS,VAX,1,0)
      VPOS = VPOS + VEL1
      IF (VPOS.LE.XMAX) GO TO 800
      CALL PLOT(XMAX,VAX,1,0)
C LABEL VELOCITY AXIS AT VLMK,0. AND VHMK
      VPOS = CG - .04/XSCAL
      CALL SYMBOL(VPOS,VAX-YXDIS,0.,.16,1,1H0)
      VPOS = CG + VLMK * VEL1
      ENCODE (3,820,ARRAY) IVL
820   FORMAT (I3)
      CALL SYMBOL (VPOS-.32/XSCAL,VAX-YXDIS,0.,.16,3,ARRAY)
      VPOS = CG + VHMK * VEL1
      ENCODE (3,820,ARRAY) IVH
      CALL SYMBOL (VPOS-.32/XSCAL,VAX-YXDIS,0.,.16,3,ARRAY)
C
C DRAW VERTICAL LINE AT VEL =0.
C
      CALL PLOT (CG,100.,0,0)
      CALL PLOT (CG,VAX,1,0)
      IF (NOPT) 601,600
C
C THIS PART OF THE CODE DRAWS THE PLOT OF INTENSITY VS VELOCITY WITH THE 00431
C VELOCITY AXIS CALIBRATED WITH 1MM/SEC = .5 INCHES.
C
C BEGIN BY ESTABLISHING THE CONSTANTS FOR COMLOT.
C
601   VDIS = VELMAX - VELMIN
      VSCAL = .5
      CALL SCALE (VSCAL,YSCAL,14.,1.,VELMIN,YMIN)
      XXDIS = .32/VSCAL
      XYDIS = .64/VSCAL
C
C LABEL VELOCITY AXIS.

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OS3 FORTRAN VERSION 3.13 MOSSRED 02/12/78 1659

```

C      ENCODE (4,380,ARRAY) VLMK
380    FORMAT (F4.1)
      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,1,8)
      VPOS = VPOS + 1.
      IF (VPOS.LE.VELMAX) GO TO 870
      CALL PLOT (VELMAX,YMIN,1,0)

C      DRAW Y-AXIS.
C
C      CALL PLOT (0.0,YMIN,0,0)
      YP=IYP
      YP=YP+.5
      IF (IYP.NE.IPP) 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
      CALL PLOT (0.0,YP,1,5)
420    CALL PLOT (0.0,YMAX,1,0)

C      LABEL Y-AXIS.
C
C      ENCODE (3,310,ARRAY) YLMK
      CALL SYMBOL (-XYDIS,YLMK-YYDIS,0...16,3,ARRAY)
      ENCODE (3,310,ARRAY) YHMK
      CALL SYMBOL (-XYDIS,YHMK-YYDIS,0...16,3,ARRAY)
      ENCODE (72,110,ARRAY) (TEXT(I),I=1,9)
      CALL SYMBOL (VELMIN,YMAX,0...12,72,ARRAY)

C      DRAW DATA POINTS WITH SMALL CIRCLES AS DATA MARKS.
C
      VPOS = VELMIN
      CALL POINTS
      DO 430 I=NZERO1,NTOT
      CALL PLOT (VPOS,RDAT(I),1,27)
430    VPOS = VPOS +VELC
600    CALL PLOTEND
      CALL UNEQUIP (20)
      ENDFILE 16
      GO TO 90
      END

```

OS3 FORTRAN VERSION 3.13

02/12/78 1659

```
      SUBROUTINE BKGCOR(RDAT,NTOT,AVG1,AVG2,NZER01)
C*****
C      PROGRAM TO CORRECT THE BACKGROUND OF A MOSSBAUER SPECTRA
C      FOR SLOPE IN THE BACKGROUND BY A RATIO METHOD
C*****
      DIMENSION RDAT(1200)
C
      AVE1= AVG1/5.
      AVE2= AVG2/5.
      DEL=AVE2-AVE1
      DELT = AVE2 * (NTOT-9-NZER01)
      DELTA = DEL/DELT
      DO 60 I=NZER01,NTOT
      RDAT(I)=RDAT(I)*{1.-(I-1)*DELTA}
60    CONTINUE
      AVG2=AVG1
      RETURN
      END
```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

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      PROGRAM SHMPLOT
C SHMPLOT 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))
C   2.) LORENTZIAN MODEL 1
C   3.) LORENTZIAN MODEL 2
C   4.) HYPERFINE MODEL CALCULATED FROM H(EFF),E**2*Q*Q,...
C   5.) 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)
C   2. PLOT DATA
C   3. DRAW Y AXIS
C   4. PLOT LORENTZIAN MODEL 1
C   5. PLOT LORENTZIAN MODEL 2
C   6. PLOT HYPERFINE MODEL
C   7. PLOT THEORETICAL SPECTRA
C   8. ADVANCE TO NEW PLOTTING REGION AND RETURN TO STEP 2
C
C TO INITIALIZE THE PROGRAM THE USER MUST PROVIDE THE FOLLOWING
C
C   NCOL = NUMBER OF COLUMNS OF PLOTS (MAX OF 2)
C   NPLTS = NUMBER OF PLOTS PER COLUMN (MAX OF 15)
C   NTYPE = PLOTTER CHOICE PARAMETER. IF NTYPE=0, THE
C           CALCOMP PLOTTER IS USED, IF NTYPE = 3, THE SMALL
C           GERBER PLOTTER IS USED
C   XSIZE = LENGTH OF X AXIS IN INCHES (DEFAULT = 10.)
C   YSIZ = LENGTH OF Y AXIS IN INCHES (DEFAULT = 4.)
C   CHARSZ = SIZE OF CHARACTERS IN LABELS (DEFAULT = .32)
C   BIASF = SPACING BETWEEN TOP OF ONE PLOT AND BOTTOM OF NEXT.
C           (DEFAULT = .2 INCHES)
C   XLOW = LOW VALUE OF X ALLOWED
C   XHIGH = HIGH VALUE OF X ALLOWED
C   XINC = INCREMENT FOR TICS ON X AXIS (STARTING FROM ZERO)
C   NLBL = LABELING FREQUENCY. IF NLBL = 1, EVERY TIC IS LABELED
C           IF NLBL=2 EVERY OTHER TIC IS LABELED STARTING AT 0.....
C   FMT = FORMAT OF THE THEORETICAL SPECTRA
C           (EG.(6(F4.0,F8.3)))
C
C OPTIONS AND OPTION FLAGS
C   IF ANY OF THE OPTION PARAMETERS ARE NON-ZERO THE OPTION
C   IS INITIATED AND THE CARDS NECESSARY FOR THAT OPTION
C   WILL BE READ
C
C OPTION FLAGS
C
C   NDAT CALLS SUBROUTINE DATPLOT
C   NLREN1 CALLS SUBROUTINE PNLREN1
C   NLREN2 CALLS SUBROUTINE PNLREN2
C   NHEFF CALLS SUBROUTINE P2
C   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.

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OS3 FORTRAN VERSION 3.13

01/11/78 0053

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C
C
C
C THE FOLLOWING INPUT CARDS ARE NECESSARY TO RUN THE PROGRAM
C IF ANY OPTIONS ARE USED THE INPUT PARAMETERS ARE LISTED IN THE
C SUBROUTINE FOR THAT OPTION
C
C*****
C
C***INPUT CARDS***
C
C   CARD 1 (3I5)
C       COLUMN
C           1 - 5   NCOL
C           6 - 10  NPLTS
C           11 - 15 NTYPE
C
C   CARD 2 (4F10.5)
C       COLUMN
C           1 - 10  XSIZE (LEAVE BLANK FOR DEFAULT)
C           11 - 20 YSIZ (DITTO)
C           21 - 30 CHARSZ (DITTO)
C           31 - 40 BIASF (DITTO)
C
C   CARD 3 (3F10.5,I5)
C       COLUMN
C           1 - 10  X LOW
C           11 - 20 X HIGH
C           21 - 30 X INC
C           31 - 35 NLBL
C
C   CARD 4 (10A8)
C       COLUMN
C           1 - 80  FMT
C
C   CARD 5 (5I5,F5.0)
C       COLUMN
C           1 - 5   NDAT
C           6 - 10  NLREN1
C           11 - 15 NLREN2
C           16 - 20 NHEFF
C           21 - 25 NTH
C           26 - 30 T
C
C*****
C
C***RUNNING THE PROGRAM***
C
C THIS ASSUMES THAT THE PROGRAM IS BEING RUN ON OS-3 AND THAT A
C BINARY FILE OF THIS PROGRAM EXISTS AND IS CALLED BINFILE.
C THE CONTROL MODE SYMBOL ≥ WILL DENOTE THE 7/8 PUNCH ON A
C CARD.
C
C   ≥JOB,.....
C   ≥EQUIP,10=PLOT
C   ≥LABEL,10/SAVE FOR SMITH (OR WHATEVER NAME YOU CHOSE)
C   ≥FORMS,10/PT-05 PLEASE (IF YOU WANT A SPECIAL PEN ON PLOTTER)
C   ≥MFBKS = 400
C   ≥TIME=200
C   ≥LOAD,BINFILE,L=*COMPL0T

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OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

C      RUN
C      CARD 1
C      CARD 2
C      CARD 3
C      CARD 4
C      CARD 5
C      .
C      .
C      DECKS OR CARDS AS REQUIRED BY OPTIONS SPECIFIED ON ABOVE
C      CARD TYPE 5
C      .
C      .
C      CARD 5
C      .
C      .
C      DECK FOR OPTIONS ON SECOND PLOT FROM CARD TYPE 5
C      .
C      .
C      THIS IS REPEATED UNTIL ALL PLOTS ARE DONE.
C      WHICH IS NCOL * NPLTS TIMES THAT CARD TYPE 5 FOLLOWED BY
C      THE NECESSARY DECK IS USED.
C      .
C      .
C      >>
C      >LOGOFF
C*****
C
C***ACTION TAKEN BY THIS ROUTINE (OUTPUT)***
C
C***PLOTTER OUTPUT***
C
C      1.  DRAW THE X AXIS, XSIZE INCHES LONG.
C      2.  PLACE TIC MARKS ON THE X AXIS STARTING FROM ZERO AT
C          INTERVALS OF XINC.
C      3.  LABEL THE APPROPRIATE TIC MARKS.  STARTING FROM ZERO,
C          SKIPPING NLBL - 1 TIC MARKS AND LABELING THE NEXT TIC MARK,
C          UNTIL THE X AXIS HAS BEEN LABELED IN BOTH DIRECTIONS.
C      4.  IF NO LABELS ARE DESIRED, NLBL SHOULD BE SET TO A NUMBER
C          GREATER THAN THE AVAILABLE NUMBER OF TIC MARKS.  THIS IS
C          DUE TO THE FACT THAT THE LABELING OF THE AXIS AND DRAWING
C          THE AXIS WITH TIC MARKS IS DONE AT THE SAME TIME.
C          STARTING AT ZERO, THE AXIS IS DRAWN BY DRAWING THE TIC MARK
C          AND CONNECTING IT WITH THE PREVIOUS MARK.  THE PROGRAM
C          COUNTS OVER NLBL TIC MARKS AND LABELS THAT TIC MARK.  IT
C          THEN COUNTS OVER NLBL MORE TIC MARKS AND DRAW THEM
C          AND LABELS THE APPROPRIATE ONE.  THIS CONTINUES UNTIL
C          THE AXIS HAS BEEN DRAWN AND LABELED IN BOTH DIRECTIONS.
C          IF THE PROGRAM REACHES EITHER XHIGH OR XLOW BEFORE
C          COUNTING NLBL TIC MARKS, NONE ARE LABELED.
C      5.  AT THE END OF THE ROUTINE, THE X AXIS WILL BE LABELED
C          #VELOCITY (CM/SEC)# AND THE Y AXIS WILL BE LABELED
C          #RELATIVE TRANSMISSION#.
C*****
C
C***SOME ADDITIONAL COMMENTS***
C
C      1.  IF ALL OPTION FLAGS ARE ZERO A BLANK IS LEFT IN THE COLUMN
C          FOR THAT PLOT
C      2.  PLOTTING ORDER HAS THE PROGRAM STARTING WITH THE LEFT MOST

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OS3 FORTRAN VERSION 3.13

01/11/78 0053

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C      COLUMN AND THE BOTTOM PLOT. THE PLOTS ARE DONE SUCH THAT
C      THE FIRST COLUMN IS COMPLETED, THEN THE SECOND COLUMN IS
C      STARTED.
C      3. FOR EVERY PLOT, A REGION XSIZE BY YSIZ IS DEFINED. THE
C      DISTANCE BIASF IS SUBTRACTED FROM YSIZ TO DETERMINE THE
C      PHYSICAL HEIGHT OF THE PLOT. THE BLANK AREA BIASF INCHES
C      WIDE IS LEFT AT THE BOTTOM OF THE PLOT. (EG. IF YSIZ=4.,
C      AND BIASF =1., THE TOTAL HEIGHT ALLOWED FOR EACH PLOT
C      WOULD BE 4 INCHES BUT THERE WOULD BE 1 INCH BLANK AT
C      THE BOTTOM AND THE PLOT WOULD ONLY OCCUPY 3 INCHES ABOVE
C      THE BLANK AREA.)
C*****END OF COMMENT FIELD*****
      DIMENSION BCDARAY(10)
      DIMENSION REL(3),FMT(10),VEL(3)
      DATA (REL = 214RELATIVE TRANSMISSION)
      DATA (VEL=174VELOCITY (CM/SEC))
      COMMON/ONE/XLOW,XHIGH,BIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
10     FORMAT (5I5,F5.0)
15     FORMAT(4F10.5)
20     FORMAT (3F10.0,I5)
30     FORMAT(10A3)
C
C OFFX AND OFFY ARE OFFSETS IN THE X AND Y DIRECTIONS FOR THE PLOTS
C
      OFFX=2.
      OFFY=2.
C
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
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
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
      PLTHT=NPLTS*YSIZ
      XFACT=XSIZE/DELX
      CALL PLOTTYPE(NTYPE)
      CALL SIZE (XSIZ,PLTHT+8.)
C
C OFFSET FOR DRAWING LABEL ON X AXIS
C
      XXOFF = CHARSZ/(XFACT*2.)
      XYOFF=1.5*CHARSZ
C
C OFFSET IN X DIRECTION FOR POSITIONING THE PHRASE #T =....#
C ON PLOT

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OS3 FORTRAN VERSION 3.13 SWMPLOT 01/11/78 0053

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C      XTOFF=XHIGH-(7.*CHARSZ/XFACT)
C
C      OFFSET IN X DIRECTION FOR TITLE OF PLOT
C
C      XLOFF = XLOW + (CHARSZ/XFACT)
C
C      OFFSET FOR WRITING A ZERO ON X AXIS
C
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.
C      XOFF99 = 2.5*CSIZN/XFACT
C
C      START DRAWING THE X AXIS
C
C      XOFF=OFFX
C      YOFF=OFFY
C      DO 100 M=1,NCOL
C      CALL SCALE(XFACT,1.,XOFF,YOFF,XLOW,0.)
C      XP=0.
C      XPT=XHIGH
C
C      DRAW THE ZERO ON THE X AXIS
C
C      CALL SYMBOL (ZXOFF,-XYOFF,0.,CHARSZ,1,1H0)
C
C      DRAW THE CENTER OR ZERO POINT ON X AXIS
C
C      CALL PLOT (0.,0.,0,0)
C      CALL PLOT (0.,0.,1,8)
C
C      START LOOP TO DRAW THE POSITIVE THEN NEGATIVE SIDE OF THE X AXIS
C
C      DO 130 M2=1,2
C      IF (XINC.EQ.0.) GO TO 120
105   DO 110 M1=1,NL3L
C      XP=XP+XINC
C      IF (ABS(XP).GT.ABS(XPT)) GO TO 120
110   CALL PLOT (XP,0.,1,8)
C      CALL LABELS (XP,BCDARRAY,NCHAR)
C      CALL SYMBOL(XP-XXOFF*NCHAR,-XYOFF,0.,CHARSZ,NCHAR,BCDARRAY)
C      CALL PLOT(XP,0.,0,0)
C      GO TO 105
120   CALL PLOT (XPT,0.,1,8)
C      CALL PLOT(0.,0.,0,0)
C      XP=0.
C      XINC=-XINC
130   XPT= XLOW
100   XOFF=XOFF+XSIZE+OFFX+OFFX
C
C      START OF PLOTTING OF THE OPTIONS
C      IFLAG IS FLAG WHICH IS ZERO IF P2 HAS NOT BEEN USED
C      AND ONE IF P2 HAS BEEN USED
C
C      IFLAG = 0
C      XOFF=OFFX
C      DO 200 M=1,NCOL

```

OS3 FORTRAN VERSION 3.13 SWMPLOT 01/11/78 0053

```

      DO 202 L=1,NPLTS
        H=0.
        SCAL = 0.
C
C READ OPTION CARD
C THE ALL IMPORTANT PARAMETER SCAL IS DESCRIBED IN SUBROUTINE
C DATPLOT
C
      READ 10,NDAT,NLREN1,NLREN2,NHEFF,NTH,T
      IF (NCAT.NE.0) CALL DATPLOT(SCAL,M,L,XLOFF,CSIZN,XOFF99)
      CALL YAXIS (SCAL)
      IF (NLREN1.NE.0) CALL PNLREN1(SCAL,NLREN1,M,L)
      IF (NLREN2.NE.0) CALL PNLREN2(SCAL,NLREN2,M,L)
      IF (NHEFF.NE.0) CALL P2(H,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
C PRINT PHRSAES #RELATIVE TRANSMISSION# AND #VELOCITY (CM/SEC)#
C ON PLOTS
C
      DO 400 M=1,NCOL
        CALL SCALE(1.,1.,XOFF,YOFF,0.,0.)
        CALL SYMBOL(-OFFX/2.,(PLTHT-21.*CHARSZ)/2.,90.,
1CHARSZ,21,REL)
        CALL SYMBOL((XSIZE-17.*CHARSZ)/2.,-CHARSZ*4.,0.,CHARSZ,17,VEL)
400  XOFF=XOFF+XSIZE+OFFX+OFFX
        CALL PLOTEND
      END

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

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 IF NO AUTISCALING 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
C     CARD 1 (10A8)
C           COLUMN
C           1 - 80 TITLE
C
C     CARD 2 (4F10.5,2I5)
C           COLUMN
C           1 - 10 YMAX
C           11 - 20 YMIN
C           21 - 30 CG
C           31 - 40 CALCON
C           41 - 45 NPTS
C           46 - 50 NZERO
C
C     CARD 3 - A (6(4X,F8.3))
C           THE DATA AS PROVIDED BY MOSSRED
C
C *****END OF COMMENT FIELD*****
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)

```

OS3 FORTRAN VERSION 3.13 DATPLOT 01/11/78 0053

```

80  FORMAT(4F10.5,2I5)
60  FORMAT (6(4X,F8.3))
70  FORMAT(10A8)
90  FORMAT (# PLOT #,I2,# COLUMN #I2,/,1X,10A8,/,
1    /,5X,#YMAX      = #F10.5,
2    /,5X,#YMIN      = #F10.5,
3    /,5X,#CG        = #F10.5,# CHANNELS#,
4    /,5X,#CALCON     = #F10.8,# MM/SEC/CH#,
5    /,5X,#NPTS       = #I10,
6    /,5X,#NZERO      = #I10,/)
    READ 70,(TITLE(I),I=1,10)
    READ 80, YMAX,YMIN,CG,CALCON,NPTS,NZERO
    NZRO1=NZERO+1
    IF(NPTS.EQ.0) RETURN
    READ 60, (Y(I),I=1,NPTS)
    IF (YMAX.EQ.0.) CALL MINMAX(Y(NZRO1),YMIN,YMAX,NPTS-NZERO)
    PRINT 90,L,M,TITLE,YMAX,YMIN,CG,CALCON,NPTS,NZERO
    DELY=(YMAX-YMIN)/(1.-BIASF)
    YFACT=Ysiz/DELY

C
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 AMMOUNT 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 PLREN2 AS TO HOW SCAL AND
C  BIASF ARE USED.
C  IF SCAL IS SET TO 0. WHEN YAXIS 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
    XH=(NPTS-CG)*CALCON
    XP=XL

C
C  SEARCH FOR THE FIRST DATA POINT THAT IS IN THE PLOTTING REGION
C
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

```

OS3 FORTRAN VERSION 3.13 DATPLOT 01/11/78 0053

```

      XP=XH
C
C SEARCH FOR THE LAST DATA POINT WITH VELOCITY LE XHIGH. NH CONTAINS
C THE INDEX FOR THAT POINT
C
      DO 280 I=1,NPTS
      NH=I
      IF (XP.LE.XHIGH) GO TO 290
280   XP=XP-CALCON
290   NH=NPTS-NH+1
      CALL PLOT (X,Y(NL),0,0)
C
C PLOT THE DATA
C
      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(SCAL.EQ.0.) RETURN
      YOFF99 = CSIZN/(2.*YFACT)
      CALL SYMBOL (XLOW-1.2*XOFF99,100.-YOFF99,0.,CSIZN,3,3H100)
      IF(YMIN.LE.99.) CALL SYMBOL (XLOW - XOFF99,99.-YOFF99,
10..CSIZN,2,2H99)
      RETURN
      END

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

      SUBROUTINE PNLREN1(SCAL,LREN,M,L)
C   THIS SUBROUTINE PLOTS LORENTZIAN 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
C   INPUT PARAMETERS
C
C   CARD 1: (F10.5)
C           COLUMN
C           1 - 10  BKG  (ARBITRARY UNITS)
C
C   CARDS 2 - LREN + 1: (3F10.5)
C           COLUMN
C           1 - 10  HT
C           11 - 20 GAM  (IN CHANNELS)
C           21 - 30 POS  (IN CHANNELS)
C
      DIMENSION HT(15),GAM(15),POS(15)
      COMMON/ONE/XLOW,XHIGH,BIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
      COMMON/TWO/CALCON,CG,NL,XL,NH,XH,YMIN
20    FORMAT (3F10.5)
91    FORMAT (2=FOR PLOT ,I3,/, COLUMN ,I3,/,9X, ,LREN,15X, ,AREA,/)
92    FORMAT (10X,I2,9X,E18.10)
      PI2 = 2.*ATAN(1.)
      PRINT 91,L,M
      READ 20, BKG
      DO 208 K=1,LREN
      READ 20, HT(K),GAM(K),POS(K)
      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
208   PRINT 92,K,AREA
      X=XL
      YCALC=BKG-YLREN(LREN,HT,GAM,POS,X)
      CALL PLOT(X,YCALC,0,0)
      DO 520 K1=NL,NH
      CALL PLOT(X,YCALC,1,0)
      X=X+CALCON
520   YCALC=BKG-YLREN(LREN,HT,GAM,POS,X)
      DO 530 K2=1,LREN
      CALL PLOT(POS(K2),BKG,0,0)
      CALL PLOT (POS(K2),BKG,1,6)
530   CALL PLOT (POS(K2),BKG-HT(K2),1,6)
      RETURN
      END

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

      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 BKG = 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
      C       
$$F(I) = BKG - (SUM(J))(HT(J)*GAM(J)/(OMEGA(I,J)**2+GAM(J)**2))$$

      C
      C NOTE THAT THIS MODEL IS NOT RESTRICTED TO ONLY THE OUTPUT FROM
      C LUCK BUT CAN BE USED BY ANY SYSTEM USING THIS MODEL
      C
      C*****
      C***INPUT PARAMETERS***
      C
      C   LREN = NUMBER OF LORENTZIANS TO BE SUMMED OVER. THIS WILL BE
      C           EITHER 32 OR 96. THIS IS SPECIFIED ON THE OPTION CARD AS
      C           DESCRIBED IN THE MAIN PROGRAM.
      C   DELE = THE ISOMER SHIFT FOR THE SPECTRA. LUCK HAS NO PROVISION
      C           FOR ISOMER SHIFT SO IT IS ADDED HERE.
      C   NPTS = THE NUMBER OF POINTS TO BE PLOTTED (MAX OF 512)
      C   HT(I) = THE HEIGHT OF THE PEAK
      C   POS(I) = THE POSITION OF THE PEAK IN CM/SEC
      C   GAM(I) = THE HALF-WIDTH AT HALF MAXIMUM OF THE PEAK IN CM/SEC
      C
      C*****
      C
      C***INPUT CARDS***
      C
      C   CARD 1 (F10.5,I5)
      C           COLUMN
      C           1 - 10 DELE
      C           11 - 15 NPTS
      C
      C   CARDS 2 - LREN + 1 (3F10.5)
      C           COLUMN
      C           1 - 10 HT(I)
      C           11 - 20 POS(I)
      C           21 - 30 GAM(I)
      C
      C   DIMENSION HT(96),GAM(96),POS(96)
      C   DIMENSION VEL(512),SPEC(512)
      C   COMMON/ONE/XLOW,XHIGH,BIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
      C   FORMAT (3F10.5)
      C   FORMAT (F10.5,I5)
      C   READ 30,DELE,NPTS
      C   DO 208 K=1,LREN
      C   READ 20, HT(K),POS(K),GAM(K)
      C   POS(K) = POS(K) + DELE
      C
      C 208 CONTINUE
      C   BKG=100.

```


OS3 FORTRAN VERSION 3.13 PNLREN2 01/11/78 0053

```
      VELINC= (XHIGH - XLOW)/FLOAT(NPTS-1)
      VEL(1) = XLOW
      DO 500 I=2,NPTS
500    VEL(I) = VEL(I-1) +VELINC
      DO 600 I=1,NPTS
      SPEC(I) = BKG
      DO 600 J=1,LREN
      IF(HT(J).EQ.0.) GO TO 600
      OMEGA = VEL(I) - POS(J)
      SPEC(I) = 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 (XFACT,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
```

OS3 FORTRAN VERSION 3.13

01/11/79 0053

```

      SUBROUTINE PLOTTH(SCAL,FMT,NTH)
C
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 LORENTZIAN
C
C   ACTION OF PROGRAM
C       1. READ IN SCALING CARD FOR Y DATA TYPE. THIS SHOULD BE
C          CREATED BY PROGRAM THAT GENERATED Y DATA.
C       2. READ IN Y DATA TYPE SPECTRA
C       3. DETERMINE IF LORENTZIAN ADD MIXTURES
C          ARE TO BE MIXED IN (NTH GREATER THAN 1).
C       4. READ IN INFORMATION CONCERNING LORENTZIAN.
C       5. DETERMINE AREAS UNDER ALL CURVES AND USE WEIGHTING
C          FACTORS TO WEIGHT THEM.
C       6. ADD THE SPECTRA TOGETHER AND PLOT.
C
C   THE PROGRAM READS IN ONLY ONE SET OF Y DATA, AND NTH = 1
C   SETS OF LORENTZIAN SPECTRA. EACH LORENTZIAN SPECTRA MAY
C   BE COMPOSED OF UP TO TEN PEAKS.
C
C *****
C
C   INPUT PARAMETERS
C
C   CARD 1: (4F10.5,I5)
C       COLUMN
C       1 - 10   YMIN      LOW VALUE OF Y AXIS
C       11 - 20  YMAX      HIGH VALUE OF Y TYPE DATA
C       21 - 30  XL        LOW VALUE OF X AXIS OF Y TYPE DATA
C       31 - 40  XH        HIGH VALUE OF X AXIS OF Y TYPE DATA
C       41 - 45  NPTS      NUMBER OF Y DATA POINTS
C
C   CARD 2 - A: (FMT)   Y TYPE DATA FOR THEORETICAL SPECTRA
C
C   CARD 3: (I10,F10.5)
C       COLUMN
C       1 - 10   LREN      NUMBER OF LORENTZIAN IN THIS SPECTRA
C       11 - 20  FACT      WEIGHTING FACTOR FOR THIS SPECTRA
C                          (DECIMAL FRACTION)
C
C   CARD 4 - A: (3F10.5) REPEAT LREN TIMES
C       COLUMN
C       1 - 10   HT        HIGHT OF PEAD DOWN FROM BACKGROUND
C       11 - 20  GAM       FULL WIDTH AT HALF MAX IN CM/SEC
C       21 - 30  POS       POSITION OF LINE IN CM/SEC
C
C   NOTE: CARD TYPES 3 AND 4 ARE REPEATED AS A SET NTH -1 TIMES
C
C *****
C
C   THE WEIGHTING FACTOR FOR THE Y TYPE DATA IS
C       FACT(Y TYPE) = 1. - SUM OF FACT(LREN TYPE)
C
C   THE PERCENTAGE AREA UNDER THE FINAL CURVE DUE TO ANY SINGLE
C   CONTRIBUTION IS FACT * 100. OF THE TOTAL AREA.
C
C   COMMON/ONE/XLOW,XHIGH,BIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
C   DIMENSION Y(5,512),X(512),YC(512),POS(10),GAM(10),HT(10),FACT(10)

```

OS3 FORTRAN VERSION 3.13 PLOTTH 01/11/78 0053

```

      DIMENSION FMT(10)
10    FORMAT (I10,F10.5)
80    FORMAT (4F10.5,2I5)
      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
C   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
C   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(NL) = XL
      PRINT 30,NTH,NL,NH,XL,XH,XINC
30    FORMAT(//,2X ENTERING PLOTTH WITH NTH = ,I5,/,
1      1      2X PARAMETERS ARE:2X
2/,      2X NL = ,I5,/,
3      3      2X NH = ,I5,/,
4      4      2X XL = ,F10.5,/,
5      5      2X XH = ,F10.5,/,
6      6      2X XINC=,F10.7)
C
C   DETERMINE AREA UNDER CURVE FOR Y DATA TYPE SPECTRA
C   AND ESTABLISH X AXIS
C
      SUMT = YMAX - Y(1,NL)
      DO 100 I = NL1,NH
      X(I) = X(I-1) + XINC
100   SUMT = SUMT + YMAX - Y(1,I)
      SUM = SUMT
      FACT(1) = 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,LREN,FACT(JJ)
      PRINT 40,JJ,LREN,FACT(JJ)
40    FORMAT (//,2X FOR MIXING COMPONENT #I2# COMPOSED OF #I2
1      1# LORENTZIAN, WITH A WEIGHTING FACTOR OF #F10.5,//
2      1# LORENTZIAN PARAMETERS#,/,T10,2X HEIGHT#,T25,2X HALF-WIDTH#,
3      3T40,2X POSITION#)
C
C   CALCULATE FACT FOR Y DATA TYPE SPECTRA

```

OS3 FORTRAN VERSION 3.13 PLOTTH 01/11/78 0053

```

C      FACT(1) = FACT(1) - FACT(JJ)
C
C      READ IN INFO FOR THE NTH SPECTRAS LREN PEAKS
C
      DO 370 L = 1,LREN
      READ 80,HT(L),GAM(L),POS(L)
      PRINT 50,HT(L),GAM(L),POS(L)
      GAM(L) = (GAM(L)/2.)**2
370    GAM(L) = 1.0/GAM(L)
50    FORMAT (10X,E10.3,5X,E10.3,5X,E10.3)
      SUMT = 0.
C
C      CALCULATE OUT LORENTZIAN SPECTRA FOR SPECTRA NUMBEEF NTH
C
      DO 380 J=NL,NH
      YL = - YLREN(LREN,HT,GAM,POS,X(J))
      Y(JJ,J) = YL
C
C      ACCUMULATE AREA OF SPECTRA JJ
C
380    SUMT = SUMT -YL
      FACT(JJ) = FACT(JJ)/SUMT
390    CONTINUE
400    CONTINUE
      FACT(1) = FACT(1)/SUM
      DO 500 I = NL,NH
      Y(1,I) = Y(1,I) - YMAX
C
C      ADD SPECTRA TOGETHER USING FACT WEIGHTING FACTORS
C
      YC(1) = 0.
      DO 500 J = 1,NTH
500    YC(1) = YC(1) + Y(J,1) * FACT(J)
C
C      RESCALE ADD MIXTURE AND PLOT
C
      CALL MINMAX(YC(NL),YMIN,YMAX,NH-NL+1)
      YFACT = SCAL/(YMAX - YMIN)
      CALL SCALE (XFACT,YFACT,XOFF,YOFF+BIASF*YSIZ,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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

SUBROUTINE P2(H,SCAL,IFLAG,M,L)
C  GENERAL NGR 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
C
C  DEFINITIONS OF INPUT PARAMETERS
C
C  HAFWIT=HALF-WIDTH AT HALF MAXIMUM OF ABSORPTION LINE,CM/SEC
C  XM0=GROUND STATE MAGNETIC G-VALUE
C  GR=RATIO OF EXCITED TO GROUND STATE GAVALUES G1/G0
C  EG=ENERGY OF NUCLEAR GAMMA RAY TRANSITION
C  OM1=SQUARE OF M1 MIXING COMPONENT
C  OE2=SQUARE OF E2 MIXING COMPONENT
C  OS0=SQUARE OF E2/M1 MIXING RATIO
C
C  D1,D2,D3,D4=EXPERIMENTALLY DET.D. ENERGY LEVELS FOR I=3/2 STATE,
C  D1 IS THE LARGEST EIGENVALUE AND THEY ARE ASSUMED TO HAVE
C  CENTROID AT ZERO VELOCITY
C  H,P10,ETA0,A0,B0,DELE=INITIAL HYPERFINE PARAMETERS
C  H= HYPERFINE FIELD IN KOE
C  DELE=ISOMER SHIFT IN CM/SEC
C  P10=QUADRAPOLE SPLITTING (INCLUDING ASYMMETRY PARAMETER) CM/SEC
C  ETA0=ASYMMETRY PARAMETER
C  A0=AZIMUTHAL ANGLE OF H W.R.T. EFG PRIN. AXIS SYSTEM
C  B0=POLAR ANGLE ETC
C  NO3=NUMBER OF COMPARISONS OF THEORY AND EXPERIMENT TO BE MADE
C  AT,BT=ORIENTATION OF UNPOLARIZED GAMMA RAY BEAM W.R.T. EFG
C  PRINCIPAL AXIS SYSTEM.
C  MO3=0 FOR POLYCRYSTALLINE SPECTRUM; POSITIVE VALUE FOR SINGLE XTAL
C  DP1,DETA,DA,OB=INCREMENTAL CHANGES IN QUAD SPLITTING,ASYMMETRY
C  PARAM, SPH POLAR COORDS, RESP.
C  KCP=CONTROL INTEGER FOR INTEGRATION OPTION
C  0 GIVES INTEGRATION OPTION
C  1 GIVES COMPARISON OPTION
C  NA= NUMBER OF PHI ANGLES IN FIRST QUADRANT OVER
C  WHICH INTEGRATION IS PERFORMED (EQUAL INCREMENTS)
C  NB= SAME AS NA EXCEPT REFERS TO THETA
C  NB=SAFE AS NA EXCEPT REFERS TO THETA
C  NX=NUMBER OF PLOT POINTS
C  NUCLEAR MAGNETON=(94.987E-3)KEV-CM/(KOE/SEC)
C
C*****
C
C***INPUT CARDS***
C
C  CARD 1 (20X,F10.5,I5)
C      COLUMN
C      21 - 30  HAFWIT
C      31 - 35  NX
C
C  CARD 2 (5F10.4)
C      COLUMN
C      1 - 10  XM0
C      11 - 20  GR
C      21 - 30  EG
C      31 - 40  OM1
C      41 - 50  OE2
C
C  CARD 3 (4F10.4)
C      COLUMN

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

C          1 - 10  D1
C          11 - 20  D2
C          21 - 30  D3
C          31 - 40  D4

```

```

C          CARD 4 (3I5)
C          COLUMN
C          1 - 5   NAH
C          6 - 10  NBH
C          11 - 15 KCP

```

```

C          CARD 5 (6F10.4)
C          COLUMN
C          1 - 10   H
C          11 - 20  P10
C          21 - 30  ETA0
C          31 - 40  A0
C          41 - 50  B0
C          51 - 60  DELE

```

```

C          CARD 6 (I5,F15.4,F10.4,I5)
C          COLUMN
C          1 - 5   NOB
C          6 - 10  AT
C          21 - 30  BT
C          31 - 35 NOB

```

```

C          CARD 7 (4F10.4)
C          COLUMN
C          1 - 10  DP1
C          11 - 20 DETA
C          21 - 30 DA
C          31 - 40 DB

```

```

C *****
C *****IMPORTANT*****
C *****

```

```

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

```

```

C *****
COMMON/ONE/XL,XRR,9IASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
DIMENSION SMGI(10),SMI(36)
DIMENSION P(2,4),E(4),PI(2,4),EA(4),PI2(2,4),DATA(20)
DIMENSION X(401),SPEC(401),EV(8,8)
DIMENSION EA1(21),I2(2,4),A1(21),EA2(21),EA3(21),EA4(21),S11(21),D
122(21),D33(21),D44(21),AB(64),RB(64),A6(16),R4(16)
DIMENSIONR(4,4),AI(4,4),EVAL(8),EVG(4,4)
DIMENSION SMG(4,4),GVG(4,4),SM(8,8),EVEC(8,9)
EXTERNAL FL,F1R,F1I,F0R,FM1R,FM1I,FRM21,FIM21,FRM11,FIM11,FR01,FIO
*1,FR11,FI11,FR21,FI21
IF(IFLAG.EQ.1) GO TO2
IFLAG = 1
READ 150,HAFWIT,NX

```

OS3 FORTRAN VERSION 3.13 P2

01/11/78 0053

```

150  FORMAT(20X,F10.5,I5)
      READ 151,XM0,GR,EG,DM1,DE2
151  FORMAT(5F10.4)
      PRINT 170,XM0,GR,EG,DM1,DE2
170  FORMAT (6H XM0= ,F10.4/5H GR= ,F10.4/5H EG= ,F10.4/6H DM1= ,F10.4/
      *6H DE2= ,F10.4)
      READ13,D1,D2,D3,D4
13   FORMAT (4F10.4)
      XH=(XRR-XL)/FLOAT(NX-1)
      DO 93 I=1,NX
93   X(I)=XL+FLOAT(I-1)*XH
      READ 1015,NAH,NBH,KCP
1015 FORMAT(3I5)
      PRINT158,D1,D2,D3,D4
158  FORMAT(1H0,3HD1=,F10.4/1H ,3HD2=,F10.4/1H ,3HD3=,F10.4/1H ,3HD4=,F
      110.4)
      L1=0
2    CONTINUE
      PRINT 3,L,M
3    FORMAT(21 CALCULATED SPECTRA FOR PLOT#,I3,5X,#COLUMN#,I3,///)
      READ15,M,P10,ETA0,A0,B0,DELE
15   FORMAT (6F10.4)
      DATA(1)=M
      DATA(2)=P10
      DATA(3)=ETA0
      DATA(4)=A0
      DATA(5)=B0
      SAV=100.
      READ 113,N08,AT,GT,M08
113  FORMAT(I5,F15.4,F10.4,I5)
      DATA(6)=N08
      DATA(7)=AT
      DATA(8)=GT
      DATA(9)=M08
      M08=FLOAT(N08)
      READ 17,D0P1,DETA,DA,DB
17   FORMAT (4F10.4)
      DATA(10)=D0P1
      DATA(11)=DETA
      DATA(12)=DA
      DATA(13)=DB
      YMIN=0.
      YMAX=[.
      IF(KCP) 1010,1010,1011
1011 CONTINUE
C    BEGIN COMPARISON LOOP
      DO 260 I6=1,N08
      S11(I6)=D1
      D22(I6)=D2
      D33(I6)=D3
260  D44(I6)=D4
      DO 7 K8=1,N08
      P1=P10+FLOAT(K8-1)*D0P1
      ETA=ETA0+FLOAT(K8-1)*DETA
      A=A0+FLOAT(K8-1)*DA
      B=B0+FLOAT(K8-1)*DB
      CALL HEX(H,P1,ETA,A,B,SM,XM0,GR,EG,WH,WE)
      CALL HGR(H,A,B,XM0,EG,SMG)
      NSG=4
      NSE=8

```

OS3 FORTRAN VERSION 3.13 P2

01/11/78 0053

```

      NCON=0
      CALL CI8(SM,SMI)
      CALL EIGEN(SMI,EVEC,NSE,NCON)
      CALL IC8(SMI,SM)
      CALL CI4(SMG,SMGI)
      CALL EIGEN(SMGI,GVG,NSG,NCON)
      CALL IC4(SMGI,SMG)
      PRINT 220, (SM(I,I),I=1,8)
220  FORMAT(1H0,8F12.5)
      PRINT 230, (SMG(I,I),I=1,4)
230  FORMAT(1H0,4F12.5)
      DO10I=1,8
10   EVAL(I)=SM(I,I)
      EA1(K8)=SM(2,2)
      EA2(K8)=SM(4,4)
      EA3(K8)=SM(6,6)
      EA4(K8)=SM(8,8)
      CHI=(EA1(K8)-D1)**2 + (EA2(K8)-D2)**2+(EA3(K8)-D3)**2+(EA4(K8)-D4)
1**2
      CHI=SQRT (CHI)
      IF(MO3.GT.1.) GO TO 326
      GO TO 325
326  IF(CHI.LT.SAV) GO TO 27
      GOTO28
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   EA(I)=SM(2*I,2*I)
      HZ=H
      P1Z=P1
      ETAZ=ETA
      AZ=A
      BZ=B
      ATZ=AT
      BTZ=BT
      WHZ=WH
      WEZ=WE
28   CONTINUE
7    CONTINUE
      DO20I=1,4
      P(1,I)=EA(I)-E01
20   P(2,I)=EA(I)-E02
      DATA(14)=WHZ
      DATA(15)=WEZ
      DATA(16)=P1Z
      DATA(17)=ETAZ
      DATA(18)=AZ
      DATA(19)=BZ
      DATA(20)=CHI
      IF (DM1) 160,160,161
161  CONTINUE
      CALL SM1(AT,BT,EV,EVG,PI,MO3,DM1,F1R,F1I,F0R,FM1R,FM1I)

```


OS3 FORTRAN VERSION 3.13 P2

01/11/78 0053

```

160 CONTINUE
   IF (DE2) 162,162,163
163 CONTINUE
   CALL SE2(AT,BT,EV,EVG,PI2,MO3,DE2,FR21,FI21,FR11,FI11,FR01,FI01,F
   *RM11,FIM11,FRM21,FIM21)
162 CONTINUE
C   FORM SPECTRUM
   DO 95 I=1,NX
95   SPEC(I)=0.
   DO 35 I=1,NX
   DO35J=1,2
   DO35K=1,4
35   SPEC(I)=SPEC(I)+FL(X(I),P(J,K)+DELE,PI(J,K),HAFWIT)
      1 + FL(X(I),P(J,K)+DELE,PI2(J,K),HAFWIT)
   GO TO 1020
1010 CONTINUE
C   INTEGRATION LOOP
   DO 1023 I=1,NX
1023 SPEC(I)=0.
      NAH1=NAH+1
      NBH1=NBH+1
      XNAH=FLOAT(NAH)
      XNBH=FLOAT(NBH)
      DAR=1.57092/XNAH
      DBR=1.57092/XNBH
      MO3=1
      P1=P10
      ETA=ETA0
      DO 1000 I1=1,NAH1
      DO 1000 J1=1,NBH1
      A=(FLOAT(I1-1)/FLOAT(NAH))*90.
      B=(FLOAT(J1-1)/FLOAT(NBH))*90.
      B=3/57.2958
      SD3=SIN(B)
      B=3*57.2958
      CALL HEX(H,P1,ETA,A,3,SM,XM0,GR,EG,WH,WE)
      CALL HGR(H,A,8,XM0,EG,SMG)
      CALL CI3(SM,SMI)
      CALL EIGEN(SMI,EVEC,NSE,NCON)
      CALL IC8(SMI,SM)
      CALL CI4(SMG,SMGI)
      CALL EIGEN(SMGI,GVG,NSG,NCON)
      CALL IC4(SMGI,SMG)
      DO 21 I=1,2
      DO 21 J=1,4
      II=2*I
      JJ=2*J
21   P(I,J)=SM(JJ,JJ)-SMG(II,II)
      IF (DM1) 164,164,165
165 CONTINUE
      CALL SM1(AT,BT,EV,EVG,PI,MO3,DM1,F1R,F1I,F0R,FM1R,FM1I)
164 CONTINUE
      IF (DE2) 166,166,167
167 CONTINUE
      CALL SE2(AT,BT,EV,EVG,PI2,MO3,DE2,FR21,FI21,FR11,FI11,FR01,FI01,F
      *RM11,FIM11,FRM21,FIM21)
166 CONTINUE
      DO 39 I=1,NX
      DO 39 J=1,2
      DO 39 K=1,4

```

OS3 FORTRAN VERSION 3.13 P2 01/11/78 0053

```

      CAL1=FL(X(I),P(J,K)+DELE,PI(J,K),HAFWIT)
      CAL2=DAR*SDB*DBR
      CAL3=FL(X(I),P(J,K)+DELE,PI2(J,K),HAFWIT)
39    SPEC(I)=SPEC(I)+CAL2*(CAL1+CAL3)
      HZ=H
      P1Z=P1
      ETAZ=ETA
      AZ=A
      BZ=B
      ATZ=A
      BTZ=B
1000  CONTINUE
1020  CONTINUE
      UPLIM=0.
      DO78I=1,NX
      W=UPLIM-SPEC(I)
      IF(W)77,78,78
77    UPLIM=SPEC(I)
78    CONTINUE
      DO79I=1,NX
79    SPEC(I)=-SPEC(I)
      PRINT 399
399   FORMAT(1X THIS IS SPEC=)
      PRINT 440,(SPEC(IHH),IHH=1,NX)
440   FORMAT(1H ,10F10.4)
      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
104   FORMAT(6H DELE=,F10.6)
      PRINT 102,(DATA(I),I=1,13)
102   FORMAT(1H0,3H H=,F10.4/1H ,4HP10=,F10.4/1H ,5HETA0=,F10.4/1H ,3HA0
1=,F10.4/1H ,3H80=,F10.4/2H0 ,5H NOB=,F10.4,5H AT= ,F10.4,5H BT= ,F
210.4,5H MOB=,F10.4/1H0,4HDP1=,F10.4/1H ,6HDETA= ,F10.4/1H ,3HDA=,F
310.4/1H ,3HDB=,F10.4)
      PRINT 103,(DATA(I),I=14,20)
103   FORMAT(1H0,3HWH=,F10.4/1H ,3HWE=,F10.4/1H ,3HWP1=,F10.4/1H ,4HETA=,
1F10.4/1H ,2HA=,F10.4/1H ,2HB=,F10.4,6H CHI= ,F10.4)
      RETURN
      END

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

SUBROUTINE SM1(AT,3T,EV,EVG,PI,MOB,DM1,F1R,F1I,F0R,FM1R,FM1I)
C   THIS PROGRAM COMPUTES PROBABILITIES FOR 1/2-3/2 TRANSITIONS
C   ...M1 TYPE
DIMENSION PI(2,4),EV(8,8),EVG(4,4)
TYPE COMPLEX(4) ALP(4,4),ALG(2,2),HR1(2,4),HRM1(2,4)
TYPE COMPLEX(4) CG111,CG120,CG13M1,CG24M1,CG230,CG221
TYPE COMPLEX(4) D11,D01,DM11,D1M1,D0M1,DM1M1
TYPE COMPLEX(4) TR1(2,4),TRM1(2,4),COMP,CONJ
TYPE COMPLEX(4) C0(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)
502 FORMAT(1H ,4F12.4)
PRINT 503
503 FORMAT(= THIS IS EV=)
PRINT 504,((EV(I,J),I=1,8),J=1,8)
504 FORMAT(1H ,8F12.4)
AT=AT/57.2958
RT=RT/57.2958
XR=-.5
XI=0.
CG111= COMP(XR,XI)
XR=1./SQRT(6.)
XI=0.
CG120= COMP(XR,XI)
XR=-1./SQRT(12.)
XI=0.
CG13M1= COMP(XR,XI)
CG24M1=CG111
CG230=CG120
CG221=CG13M1
C   SET UP EIGENFUNCTION MATRIX FOR I=1/2 STATE,ALG
C   ALG(1,1)= COMP(EVG(1,2),EVG(3,2))
C   ALG(2,2)= COMP(EVG(2,4),EVG(4,4))
C   ALG(1,2)= COMP(EVG(1,4),EVG(3,4))
C   ALG(2,1)= COMP(EVG(2,2),EVG(4,2))
C   SAME FOR I=3/2 STATE,ALP
C   D0901IW=1,4
C   D0901JW=1,4
901 ALP(JW,IW)= COMP(EV(JW,2*IW),EV(JW+4,2*IW))
C   COMPUTE D-MATRIX,K=1
C   XI=F1I(AT,3T)
C   XR=F1R(AT,3T)
C   D11= COMP(XR,XI)
C   XR=F0R(3T)
C   XI=0.
C   D01= COMP(XR,XI)
C   XR=FM1R(AT,3T)
C   XI=FM1I(AT,3T)
C   DM11= COMP(XR,XI)
C   XR=-FM1R(AT,3T)
C   XI=FM1I(AT,3T)
C   D1M1= COMP(XR,XI)

```

053 FORTRAN VERSION 3.13 SM1

01/11/78 0053

```

      XR=FOR(BT)
      XI=0.
      DM1= COMP(XR,XI)
      XR=-F1R(AT,BT)
      XI=F1I(AT,BT)
      DM1M1= COMP(XR,XI)
C     SET-UP TRANSITION MATRIX CONNECTING ALP AND ALG
      DO700I=1,2
      DO700J=1,4
      HR1(I,J)=COMP(0.,0.)
700   HRM1(I,J)=COMP(0.,0.)
      HR1(1,1)=CG111*DM1
      HR1(1,2)=CG120*DM1
      HR1(1,3)=CG13M1*DM1
      HR1(2,2)=CG221*DM1
      HR1(2,3)=CG230*DM1
      HR1(2,4)=CG24M1*DM1
      HRM1(1,1)=CG111*DM1M1
      HRM1(1,2)=CG120*DM1M1
      HRM1(1,3)=CG13M1*DM1M1
      HRM1(2,2)=CG221*DM1M1
      HRM1(2,3)=CG230*DM1M1
      HRM1(2,4)=CG24M1*DM1M1
C     USE MATRIX MULTIPLICATION TO OBTAIN TRANSITION MATRIX ELEMENTS
      DO702I=1,2
      DO702J=1,4
      TR1(I,J)=COMP(0.,0.)
702   TRM1(I,J)=COMP(0.,0.)
      Z03=FLOAT(M03)
      IF (Z03.GT.0.) GO TO 720
      GO TO 719
720   CONTINUE
      DO703I=1,2
      DO703J=1,4
      DO703K=1,4
      DO 703 L=1,2
      TR1(I,J)= TR1(I,J) + CONJ(ALG(L,I))*HR1(L,K)*ALP(K,J)
703   TRM1(I,J)=TRM1(I,J) + CONJ(ALG(L,I))*HRM1(L,K)*ALP(K,J)
      DO704I=1,2
      DO704J=1,4
      X1=NORM(TR1(I,J))**2
      X2=NORM(TRM1(I,J))**2
704   PI(I,J)=CM1*(X1+X2)
      GO TO 711
C     POLYCRYSTALLINE SPECTRUM
719   DO 709 I=1,2
      DO 709 J=1,4
      C0(I,J)=CG120* CONJ(ALG(1,I))*ALP(2,J)
      1 + CG230* CONJ(ALG(2,I))*ALP(3,J)
      C1(I,J)=CG111* CONJ(ALG(1,I))*ALP(1,J)
      1 + CG221* CONJ(ALG(2,I))*ALP(2,J)
      CM1(I,J)=CG24M1* CONJ(ALG(2,I))*ALP(4,J)
      1 + CG13M1* CONJ(ALG(1,I))*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)=DM1*(X1+X2+X3)
      AT=AT*57.2958
      BT=BT*57.2958
711   CONTINUE

```

OS3 FORTRAN VERSION 3.13 SM1 01/11/78 0053

```

      PRINT 401
401  FORMAT(1X THIS IS PI)
      PRINT 440,((PI(II,JJ),JJ=1,4),II=1,2)
440  FORMAT(1H ,4F12.4)
      RETURN
      END

```

OS3 FORTRAN VERSION 3.13 01/11/78 0053

```

      SUBROUTINE HGR(H,A,B,XM0,EG,SMG)
      DIMENSION SMG(4,4)
      C CONVENTION IS THAT -1/2 CORRESPONDS TO 1, ETC
      G0=(94.987E-3)*XM0/EG
      G0=-G0*M
      DO 811 I=1,4
      DO 811 J=1,4
811  SMG(I,J)=0.
      A=A/57.2958
      B=B/57.2958
      SMG(1,1)=-.5*COS(B)*G0
      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)*G0
      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)*G0
      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

```

OS3 FORTRAN VERSION 3.13 01/11/78 0053

```

      SUBROUTINE CI8(SM,SMI)
      DIMENSION SM(8,8),SMI(36)
      DO 1 M=1,8
      IJ=(M*(M+1))/2
      MS=M
      DO 1 J=MS,8
      SMI(IJ)=SM(M,J)
1  IJ=IJ+J
      RETURN
      END

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

SUBROUTINE HEX(H,P1,ETA,A,B,SM,XM0,GR,EG,WH,WE)
DIMENSION R(4,4),AI(4,4),SM(8,8)
C  NUMBERING CONVENTION IS THAT -3/2 CORRESPONDS TO 1,ETC
X12=1.+(ETA**2)/3.
WE=.5*(P1/SQRT(X12))
WH=(94.987E-3)*XM0*GR/EG
WH=-WH*4
A=A/57.2958
B=B/57.2958
DO 1 I=1,4
DO1J=1,4
1  R(I,J)=0.
   R(1,1)=-1.5*WH*COS(B) + WE
   R(2,2)=-.5*WH*COS(B) - WE
   R(3,3)=.5*WH*COS(B) - WE
   R(4,4)=1.5*WH*COS(B) + WE
   R(1,2)=(SQRT(3.)/2.)*WH*SIN(B)*COS(A)
   R(2,1)=R(1,2)
   R(2,3)=WH*SIN(B)*COS(A)
   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(3,1)=R(1,3)
   R(2,4)=R(1,3)
   R(4,2)=R(1,3)
DO2I=1,4
DO2J=1,4
2  AI(I,J)=0.
   AI(1,2)=(SQRT(3.)/2.)*WH*SIN(B)*SIN(A)
   AI(2,1)=-AI(1,2)
   AI(2,3)=WH*SIN(B)*SIN(A)
   AI(3,2)=-AI(2,3)
   AI(3,4)=AI(1,2)
   AI(4,3)=-AI(3,4)
DO3I=1,8
DO3J=1,8
3  SM(I,J)=0.
DO5I=1,4
DO5J=1,4
5  SM(I,J)=R(I,J)
   K = I + 4
   L = J + 4
6  SM(K,L)=R(I,J)
DO6I=1,4
DO6J=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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

      SUBROUTINE SE2(A,B,EV,EVG,PI2,MOB,DE2,FR21,FI21,FR11,FI11,FR01,FI0
      *1,FRM11,FIM11,FRM21,FIM21)
C     THIS PROGRAM COMPUTES PROBABILITIES FOR 1/2-3/2 TRANSITIONS ... E2
C     TYPE
      DIMENSION PI2(2,4),EV(8,8),EVG(4,4)
      TYPE COMPLEX(4) CM2(2,4),CM1(2,4),C0(2,4),C1(2,4),C2(2,4)
      TYPE COMPLEX(4) TP1(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) CH111,CH120,CH14M2,CH212,CH221,CH230,CH24M1,CH13M1
      TYPE COMPLEX(4) DM21,DM11,D01,D11,D21
      TYPE COMPLEX(4) DM2M1,DM1M1,D1M1,D0M1,D2M1
      REAL NORM
      A=A/57.2958
      B=B/57.2958
      XR=-1./(2.*SQRT(5.))
      XI=0.
      CH111= COMP(XR,XI)
      XR=1./SQRT(10.)
      CH120= COMP(XR,XI)
      XR=-SQRT(3.)/(2.*SQRT(5.))
      CH13M1= COMP(XR,XI)
      XR=1./SQRT(5.)
      CH14M2= COMP(XR,XI)
      CH24M1=-CH111
      CH230=-CH120
      CH221=-CH13M1
      CH212=-CH14M2
C
C     COMPUTE D-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=FI01(A,B)
      D01= COMP(XR,XI)
      XR=FR11(A,B)
      XI=FI11(A,B)
      D11= COMP(XR,XI)
      XR=FR21(A,B)
      XI=FI21(A,B)
      D21= COMP(XR,XI)
      XR=-FR21(A,B)
      XI=+FI21(A,B)
      DM2M1= COMP(XR,XI)
      XR=+FR11(A,B)
      XI=-FI11(A,B)
      DM1M1= COMP(XR,XI)
      XR=-FR01(A,B)
      XI=FI01(A,B)
      D0M1= COMP(XR,XI)
      XR=+FRM11(A,B)
      XI=-FIM11(A,B)
      D1M1= COMP(XR,XI)
      XR=-FRM21(A,B)
      XI=+FIM21(A,B)
      D2M1= COMP(XR,XI)

```

OS3 FORTRAN VERSION 3.13 SE2

01/11/78 0053

```

C
C   SET UP EIGENFUNCTION MATRIX FOR I=1/2 STATE, ALG
C
  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))
C
C   SAME FOR I=3/2 STATE, ALP
C
  DO90I=1,4
  DO90J=1,4
90  ALP(JW,IW)= COMP(EV(JW,2*IW),EV(JW+4,2*IW))
C
C   DEFINE TRANSITION MATRICES
C
  DO70I=1,2
  DO70J=1,4
  HR1(I,J)=COMP(0.,0.)
70  HRM1(I,J)=COMP(0.,0.)
  HR1(1,1)=CH111*D11
  HR1(1,2)=CH120*D01
  HR1(1,3)=CH13M1*DM11
  HR1(1,4)=CH14M2*DM21
  HR1(2,1)=CH212*D21
  HR1(2,2)=CH221*D11
  HR1(2,3)=CH230*D01
  HR1(2,4)=CH24M1*DM11
  HRM1(1,1)=CH111*D1M1
  HRM1(1,2)=CH120*D0M1
  HRM1(1,3)=CH13M1*DM1M1
  HRM1(1,4)=CH14M2*DM2M1
  HRM1(2,1)=CH212*D2M1
  HRM1(2,2)=CH221*D1M1
  HRM1(2,3)=CH230*D0M1
  HRM1(2,4)=CH24M1*DM1M1
C
C   USE MATRIX MULTIPLICATION TO OBTAIN TRANSITION MATRIX ELEMENTS
C
  DO702I=1,2
  DO702J=1,4
  TR1(I,J)=COMP(0.,0.)
702  TRM1(I,J)=COMP(0.,0.)
  Z03=FLOAT(.03)
  IF(Z03.GT.0.)GOTO720
  GOT0719
720  CONTINUE
  DO703I=1,2
  DO703J=1,4
  DO703K=1,4
  DO703L=1,2
  TR1(I,J)=TR1(I,J)+ CONJ(ALG(L,I))*HR1(L,K)*ALP(K,J)
703  TRM1(I,J)=TRM1(I,J)+ CONJ(ALG(L,I))*HRM1(L,K)*ALP(K,J)
  DO704I=1,2
  DO704J=1,4
  X1=NORM(TR1(I,J))**2
  X2=NORM(TRM1(I,J))**2
704  PI2(I,J)=DE2*(X1+X2)
  GOT0711
C   POLYCRYSTALLINE SPECTRUM

```


OS3 FORTRAN VERSION 3.13 SE2

01/11/78 0053

```

719  D0709I=1,2
      D0709J=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))*AL
1P(3,J)
      C0(I,J)=CH120* CONJ(ALG(1,I))*ALP(2,J)+CH230* CONJ(ALG(2,I))*ALP(3
1,J)
      C1(I,J)=CH111* CONJ(ALG(1,I))*ALP(1,J)+CH221* CONJ(ALG(2,I))*ALP(2
1,J)
      C2(I,J)=CH212* CONJ(ALG(2,I))*ALP(1,J)
      X1=NORM(CM2(I,J))**2
      X2=NORM(CM1(I,J))**2
      X3=NORM(C0(I,J))**2
      X4=NORM(C1(I,J))**2
      X5=NORM(C2(I,J))**2
709  PI2(I,J)=0E2*(X1+X2+X3+X4+X5)
711  CONTINUE
      A=A*57.2958
      B=B*57.2958
      RETURN
      END

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

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 FRM21(A,B)
FRM21  =-.5*(1.-COS(B))*SIN(B)*COS(2.*A)
RETURN
END
```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

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

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```
FUNCTION F1I(A,B)
F1I    = .5*(1.+COS(B))*SIN(A)
RETURN
END
```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```
FUNCTION F0R(B)
F0R    =-SIN(B)/SQRT(2.)
RETURN
END
```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

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

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```
FUNCTION FM1I(A,B)
FM1I   =.5*(1.-COS(B))*SIN(A)*(-1.)
RETURN
END
```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

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

OS3 FORTRAN VERSION 3.13

01/11/78 0053

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

OS3 FORTRAN VERSION 3.13

01/11/78 0053

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

OS3 FORTRAN VERSION 3.13

01/11/78 0053

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

OS3 FORTRAN VERSION 3.13

01/11/78 0053

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

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```
FUNCTION FR01(A,B)
FR01  =-SQRT(3./2.)*SIN(B)*COS(B)
RETURN
END
```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

      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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

SUBROUTINE LABELS (VAL,ARRAY,NPRINT)
AVAL = ABS(VAL)
IF(AVAL.GE.999.995.OR. AVAL .LT. .01) GO TO 100
N = 6
ILOG = XLOG = ALOG10(AVAL)
M = 4 - ILOG
IF(XLOG.LT.0.) M = 5
IF(VAL .LT.0.) N = 7
IF(VAL.LT.0..AND.XLOG.LT.0.) N=8
NPRINT = N - M + 2
NCHAR = N
ENCODE (6,50,FMT) N,M
50  FORMAT (*(F#,I1,*,*,I1,*)*)
JJ = IFIX((AVAL+.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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

SUBROUTINE YAXIS (SCAL)
COMMON/ONE/XLOW,XHIGH,BIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
COMMON/TWO/CALCON,CG,NL,XL,NH,XH,YMIN
IF(SCAL.EQ.0.) GO TO 220
XP=XLOW
DO 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)
230  XP=XHIGH
RETURN
C
C IF NO DATA IS TO BE PLOTTED BUT THEORETICAL SPECTRA ARE,
C THE Y AXIES ARE DRAWN AT THIS POINT AND THE SCALE FACTOR
C 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.,1,0)
CALL PLOT (XLOW,SCAL,1,0)
CALL PLOT (XHIGH,0.,0,0)
CALL PLOT (XHIGH,0.,1,0)
CALL PLOT (XHIGH,SCAL,1,0)
SCAL = SCAL * (1.-BIASF)
RETURN
END

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

SUBROUTINE TANDH (SCAL,T,H,XTOFF)
COMMON/ONE/XLOW,XHIGH,BIASF,XSIZE,YSIZ,CHARSZ,XOFF,YOFF,XFACT
DIMENSION FORM(3),BCDARRAY(10)
20  FORMAT(2H =,I3)
70  FORMAT(2HT=,F4.2,I1,2)
CALL SCALE(XFACT,1.,XOFF,YOFF+BIAF*YSIZ,XLOW,0.)
IF (T.EQ.0.) GO TO 10
ILOG=ALOG10(T)
NFORM=2-ILOG
ENCODE(11,70,FORM)NFORM
ENCODE(6,FORM,BCDARRAY)T
YTOFF = SCAL/2.
CALL SYMBOL (XTOFF,YTOFF,0.,CHARSZ,6,BCDARRAY)
10  IF (H.EQ.0.) RETURN
YHOFF=SCAL/2.-(1.5*CHARSZ)
IH=H
ENCODE (6,20,BCDARRAY) IH
CALL SYMBOL(XTOFF,YHOFF,0.,CHARSZ,6,BCDARRAY)
XHOFF = XTOFF + CHARSZ/XFACT
CALL SYMBOL(XHOFF,YHOFF,0.,CHARSZ/2.,1,1HE)
RETURN
END

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

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

```

OS3 FORTRAN VERSION 3.13

01/11/78 0053

```

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

```

APPENDIX II
Program GVAL

73/74 OPT=1 TRACE

FTN 4.6+452

PROGRAM GVAL(INPUT,OUTPUT)

```

C
C THIS PROGRAM INPUTS G VALUES OBTAINED FROM THE EPR SPECTRA OF AN S
C S = 1/2 SYSTEM AND OUTPUTS THE CRYSTAL FIELD PARAMETERS D,E, AND
C THE ENERGY OF THE GROUND ELECTRONIC STATE. THE PROGRAM READS IN
C MODULUS OF THE G TENSOR AS GX,GY, AND GZ IN FREE FORM INPUT MODE
C AND PRINTS OUT ALL POSSIBLE REAL PERMUTATIONS OF THE G TENSOR
C WHICH LEAD TO REAL EIGENVECTORS. IF A GIVEN SET WILL NOT CONVERGE,
C WITHIN 50 ITERATIONS, A MESSAGE IS PRINTED OUT WHICH STATES THE
C PROBLEM. IF THE SUM GX + GY - GZ IS NEGATIVE, A REAL SET OF
C EIGENVECTORS CANNOT BE FOUND.
C
C
C      DIMENSION G(6)
C      REAL K
C      READ *,GX,GY,GZ
C      R2 = SORT(2.)
C      G(1) = GX
C      G(2) = -GX
C      G(3) = GY
C      G(4) = -GY
C      G(5) = GZ
C      G(6) = -GZ
20  FORMAT(1H1,////,3X, GX,6X, GY,6X, GZ,6X, ANORM,8X,
1    A,10X, B,10X, C,10X, K,9X, D/LAM,8X, E/LAM,
2    9X, E/D,8X, ENERGY/LAM,/)
C      PRINT 20
C
C PERMUTE ALL POSSIBLE COMBINATIONS OF G VALUES
C
C      DO 90 I = 1,6
C      GX = G(I)
C      DO 80 J = 1,6
C      GY = G(J)
C      IF(ABS(GX).EQ.ABS(GY)) GO TO 80
C      DO 70 L = 1,6
C      GZ = G(L)
C      IF(ABS(GX).EQ.ABS(GZ)) GO TO 70
C      IF(ABS(GY).EQ.ABS(GZ)) GO TO 70
C
C CHECK NORMALIZATION  A*A + B*B + C*C = ANORM
C
C IF GX+GY-GZ IS NEGATIVE, ANORM WILL ALSO BE NEGATIVE AND THIS
C CAN ONLY HAPPEN WHEN AN IMAGINARY SET OF A,B, AND C ARE OBTAINED
C SINCE A, B, C ARE SUPPOSE TO BE REAL, THIS SET IS THROWN OUT
C
C      ANORM = (GX*GX+GY*GY+GZ*GZ+GY*GZ-GX*GY-GX*GZ)/(4.*(GY+GZ-GX))
C      IF(ANORM.LT.0.) GO TO 70
C      SQRTG = SQRT(GZ + GY - GX)
C      A = (GZ + GZ + GY - GX)/(4.*SQRTG)
C      B = (GY - GX)/(2.*R2*SQRTG)
C      C = (GY + GX)/(4.*SQRTG)
C      CALL FIT1(A,B,C,K,GX,GY,GZ,IFLAG)
C      D = E = ENERGY = ED = 0.
C      IF(IFLAG.GE.0) CALL DEL(A,B,C,D,E,ENERGY)
C      IF (D.NE.0.) ED = E/D
C      PRINT 40,GX,GY,GZ,ANORM,A,B,C,K,D,E,ED,ENERGY

```


73/74 OPT=1 TRACE

FTN 4.6+452

```

40  FORMAT(1X,3(F6.3,2X),5(F9.6,2X),4(F11.7,2X),/)
70  CONTINUE
80  CONTINUE
90  CONTINUE
820  CONTINUE
    END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      SUBROUTINE DEL (A,B,C,D,E,EN)
C
C  COMPUTE CRYSTAL FIELD PARAMETERS FROM EIGENVECTOR
C
C
      DIMENSION X(3,3),Y(3),WKAREA(16)
      R2 = SQRT(2.)
      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*B)
      CALL LEQT1F (X,M,N,IA,Y,IDGT,WKAREA,IER)
      EN = Y(1)
      D = Y(2)
      E = Y(3)
      IF (IER.NE.0) PRINT 90,IER
90  FORMAT(5X,'ERROR IN SOLVING FOR D,E,AND ENERGY.  ERROR CODE = #I5)
      RETURN
    END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      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 = B/SUMR
      C = C/SUMR
    END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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
C  NORMALIZE INITIAL TRIAL
C
  CALL NORM(A,B,C)
10  CONTINUE
  AA = A*A
  BB = B*B
  CC = C*C
  AB = A*B
  AC = A*C
  BC = B*C

C
C  CAUCULATE DERIVATIVES
C
  DGXDA = 2.*(2.*C-R2*K*B)
  DGXDB = 2.*(-2.*B + R2*K*(C-A))
  DGXDC = 2.*(2.*A + R2*K*B)
  DGXDK = 2.*R2*(BC-AB)
  DGYDA = 2.*(2.*C+R2*K*B)
  DGYDB = 2.*(2.*B + R2*K*(C+A))
  DGYDC = 2.*(2.*A+R2*K*B)
  DGYDK = 2.*R2*(BC+AB)
  DGZDA = 4.*A*(1.+K)
  DGZDB = -4.*B
  DGZDC = 4.*C*(1.-K)
  DGZDK = 2.*(AA-CC)
  DONECA = 2.*A
  DONECB = 2.*B
  DONECC = 2.*C
  DONECK = 0.

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

C
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) = DGYDA

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

APARA(2,2) = DGYDB
APARA(2,3) = DGYDC
APARA(2,4) = DGYDK
APARA(3,1) = DGZDA
APARA(3,2) = DGZDB
APARA(3,3) = DGZDC
APARA(3,4) = DGZDK
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
C ACCUMULATE SUM OF SQUARE OF RESIDUALS
C
RES = 0.
DO 200 I = 1,4
200 RES = RES + PARA(I)**2
C
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 LEQT1F(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
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 = #I5)
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

73/74 OPT=1 TRACE

FTN 4.6+452

PROGRAM QSPLIT(INPUT,OUTPUT)

```

C
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
C   D,E,XLAM = CRYSTAL FIELD AND SPIN ORBIT TERMS
C   XKAP      = KAPPA USED IN CALCULATING G VALUES.  AN ORBITAL
C               REDUCTION FACTOR.
C   HYPERK    = KAPPA USED IN HYPERFINE CALCULATION.  ORIGIN SIMILAR
C               TO XKAP
C   P         = MULTIPLICATIVE FACTOR FOR HYPERFINE CALCULATION.
C               CALCULATED FROM  $G * G_N * \text{BETA}(N) * \text{BETA}(E) * \langle R^{*-3} \rangle$ 
C               COMMONLY  $P * \text{HYPERK} / (G_N * \text{BETA}(N)) = 200 \text{ KOE (APPROX)}$ 
C   XYNN,XZNN,YZNN = COVALENCY FACTORS
C   BARN      = CONSTANT IN BARNS FOR G ( $10^{*-24} \text{ CM}^{*2}$ )
C   R         = CONSTANT FOR  $\langle R^{*-3} \rangle = R * A(0)^{*-3}$ 
C               COMMONLY  $R = 5$ .
C
C THIS PROGRAM USES TWO LIBRARIES IN RUNNING. THEY ARE OBTAINED
C AND LOADED AS FOLLOWS
C
C   USER,AASA5C,.....
C   CHARGE,725160,A.
C   SETTLE,100.
C   ATTACH,IMSL/UN=LIBRARY.
C   GET,LPLTLIB/UN=AAGI3C.
C   GET,OSULIB/UN=LIBRARY.
C   GET,GVALBIN.
C   LOSET,LIB=IMSL/LPLTLIB/OSULIB.
C   GVALBIN.
C   7/8/9
C   .
C   .
C   INPUT DECK
C   .
C   .
C   7/8/9
C   6/7/8/9
C
C   DIMENSION EQQ(3),ETA(3)
C   DIMENSION H(6,6), HSO(6,6), HCF(6,6), VEC(6,6), VAL(6), WK(60)
10  FORMAT(3F10.5,/,F10.5,/,2F10.5,/,5F10.5)
20  FORMAT (/,# CRYSTAL FIELD MATRIX#,/,6(6(2X,F10.3)/))
30  FORMAT (/,# SPIN ORBIT MATRIX# ,/,6(6(2X,F10.3)/))
40  FORMAT (/,# SO + CF MATRIX#,/,6(6(2X,F10.3)/))
50  FORMAT(1H1, # D = #,F10.3,5X, # E = #,F10.3,5X, # LAMBOA = #F10.3,
1   /, # KAPPA = #F10.5,/, # HYPERK = #F10.5,5X, # P = #F10.5,/,
2   # XYNN = #F10.5,5X, # XZNN = #F10.5,5X, # YZNN = #F10.5,
3   5X, # BARN = #,F10.5,5X, # R = #F10.5)
60  FORMAT (/,6( # EIGENVALUE = #G15.8,2X#EIGENVECTOR = #

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

1  6(G14.8,1X),/,))
70  FORMAT (/,# PREFORMANCE CODE = #F10.5,5X,#ERROR CODE IER = #I5)
80  FORMAT(2I10,2F10.5)
   N = 6
   IJOB = 2
   READ 80,NCALC,NPTS,TMIN,TMAX
   DO 200 ITER = 1,NCALC
   READ 10,D,E,XLAM,XKAP,HYPERK,P,XYNN,XZNN,YZNN,BARN,R
C
C  ASSIGN DEFAULT VALUES FOR PARAMETERS LEFT AS ZERO
C
   IF(P.EQ.0.) P = .260
   IF (BARN.EQ.0.) BARN = .18
   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
C
C  START CALCULATION
C
   PRINT 50,D,E,XLAM,XKAP,HYPERK,P,XYNN,XZNN,YZNN,BARN,R
   XYN = SQRT(XYNN)
   XZN = SQRT(XZNN)
   YZN = SQRT(YZNN)
   CALL CF(HCF,D,E)
   CALL SO(HSO,XLAM)
   CALL MATAADD(HCF,HSO,H,N)
   PRINT 20, ((HCF(I,J),J=1,N),I=1,N)
   PRINT 30, ((HSO(I,J),J=1,N),I=1,N)
   PRINT 40, ((H(I,J),J=1,N),I=1,N)
   CALL VCVTFS(H,N,N,H)
   CALL EIGRS(H,N,IJOB,VAL,VEC,N,WK,IER)
   PRINT 70,WK(1),IER
   PRINT 60,(VAL(J),(VEC(I,J),I=1,N),J=1,N)
   CALL GVAL (VAL,VEC,XKAP,E/D,HYPERK,P,XYN,XZN,YZN,R,BARN,EQQ,ETA)
   CALL QSVST(VAL,EQQ,ETA,TMIN,TMAX,NPTS)
200 CONTINUE
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE MINMAX (ARRAY,NPTS,AMIN,AMAX)
DIMENSION ARRAY(NPTS)
AMIN = AMAX = ARRAY(1)
IF (NPTS.LE.1) RETURN
DO 10 I = 2,NPTS
AMIN = AMIN1(ARRAY(I),AMIN)
10 AMAX = AMAX1(ARRAY(I),AMAX)
RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE CF(HCF,D,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) = -D
HCF(2,2) = HCF(5,5) = 2. * D
HCF(1,3) = HCF(3,1) = HCF(4,6) = HCF(6,4) = 3. * E
RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE MATA00(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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE GVAL (VAL, VEC, XKAP, ED, HYPERK, P, XYN, XZN, YZN, R, BARN,
1  EQQ04, ETA)
  DIMENSION VAL(6), VEC(6,6)
  DIMENSION EQQ04(3), ETA(3)
90  FORMAT (/, # FOR DOUBLET #I2# WITH E/D =#F10.7# AND AN EIGENVALUE =
1  #, G14.8, /, # A = #G14.8, 5X, #B = #G14.8, 5X, #C = #G14.8, /,
1# GX = #G14.8, 5X, #GY = #G14.8, 5X, #GZ = #, G14.8, /,
1# AX = #G14.8, 5X, #AY = #G14.8, 5X, #AZ = #, G14.8, /,
3# EEGQ/4= #G14.8, 5X, #ETA= #G14.8)
  R2 = SQRT(2.)
  R22 = R2 * 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 = -VEC(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.
  BKR2 = XKAP * B * SQRT(2.)
  GX = (BKR2 * (C - A) + AC2 - BB) * 2.
  GY = (BKR2 * (C + A) + AC2 + BB) * 2.
  GZ = (XKAP * (AA - CC) + AA - BB + CC) * 2.

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

```


73/74 OPT=1 TRACE

FTN 4.6+452

```

      AY = P*(4.*(-C13 ) - 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 ))
C
C  CALCULATE THE QUADRUPOLE ETA AND EQQ/4 TERMS FOR ALL THREE LEVELS
C
      ETAQ = R67*((AA + CC)/2.*(XZNN-YZNN) - AC*(XZNN + YZNN))
      Q      = R27*((AA + CC)/2.*(XZNN+YZNN) - BB*(XYNN + YXNN) +
1      AC * (YZNN - XZNN))
      ETA(JJ) = ETAQ/Q
      EQQD4(JJ) = Q*BARN*2.0226/4.
C
C  BEGIN FINAL PRINT OUT
C
      PRINT 90,JJ,ED,VAL(INDEX),A,B,C,GX,GY,GZ,AX,AY,AZ,
1      EQQD4(JJ), ETA(JJ)
100 CONTINUE
      RETURN
      END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE QSVST(VAL,EQQ,ETA,TMIN,TMAX,NPTS)
DIMENSION VAL(6),EQQ(3),ETA(3),T(101),QS(101)
DT = (TMAX-TMIN)/(NPTS-1)
T(1) = TMIN
DO 10 I = 2,NPTS
10  T(I) = 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 + EQQ(I)*EXPFUN
      ETAFUN = ETAFUN + ETA(I)*EXPFUN
20  CONTINUE
      ETAT = ETAFUN/Z
      EQQT = EQQFUN/Z
      QS(J) = 2. * EQQT * SQRT(1.+(ETAT*ETAT/3.))
30  CONTINUE
      CALL MINMAX (QS,NPTS,QSMIN,QSMAX)
      CALL LPLOT (T,QS,NPTS,TMIN,TMAX,YMIN,YMAX)
      CALL AXIS (0,0,0,0.,0.,0.,0.,0.,0.,0.,0.,0.,0.,0.,0.)
      PRINT 40,((T(J),QS(J)),J=1,NPTS)
40  FORMAT(/,T10,*,T25,*,QS*,/, (5X,F10.5,5X,F10.6))
      RETURN
      END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE LPLOT (X,Y,N,XLOW,XHIGH,YMIN,YMAX)
DIMENSION LABEL1(3),LABEL2(3)
DIMENSION X(100),Y(100),LABEL(3)
DATA LABEL1/11HTEMPERATURE/,LABEL2/20HQADRUPOLE SPLITTING/
20 DELY=YMAX-YMIN
  IF (DELY.EQ.0.) DELY = 2.
  DELX=XHIGH-XLOW
  DELY2=DELY/2.
  YMAX=YMAX+DELY2
  YMIN=YMIN-DELY2
  YTIC=DELY2
  DELY2=DELY
  DELY=DELY+DELY
  XTIC=DELX/4.
  MARGY = 15
  CALL AXIS (6LOUTPUT,8,6,XTIC,DELY,XLOW,YMIN,XLOW,YMIN,
1  YTIC,6,6,MARGY,UPCX,UPCY)
  XXOFF=4.*UPCX
  XYOFF=YMIN-2.*UPCY
  YXOFF=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
30  FORMAT (E9.2)
    CALL LABLPLT (9,0,0,LABEL)
40  XPOS=XPOS+XTIC
C
C LABEL Y AXIS
C
  DO 50 I=1,5
    CALL PLOT (YXOFF,YPOS,0,1R )
    ENCODE (9,30,LABEL) YPOS
    CALL LABLPLT (9,0,0,LABEL)
50  YPOS=YPOS+YTIC
C
C PLOT DATA
C
  DO 60 I=1,N
60  CALL PLOT (X(I),Y(I),0,1R.)
    XX=XLOW+(DELX/2.)-(5.*UPCX)
    XYOFF=XYOFF-2.*UPCY
    CALL PLOT (XX,XYOFF,0,1R )
    CALL LABLPLT (11,0,0,LABEL1)
120 YPOS=YMIN+DELY2+10.*UPCY
    YXOFF=YXOFF-2.*UPCX
    CALL PLOT (YXOFF,YPOS,0,1R )
    CALL LABLPLT (20,0,1,LABEL2)
  RETURN
  END

```

APPENDIX IV
Program RELAX

73/74 OPT=1 TRACE

FTN 4.6+452

PROGRAM RELAX (INPUT,OUTPUT,PUNCH,TAPE10)
 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.

INPUT PARAMETERS AND ARRAYS

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($E^2 Q Q$)/4.
 ETA QUADRUPOLE ASSYMETRY PARAMETER
 VJ = RELAXATION RATE
 ALFA,BETA,GAMMA = EULER ANGLES FOR QUARRUPOLE TENSOR

INPUT INFORMATION

CARD 1: (2I10,2F10.5,I10)
 COLUMN
 1 - 10 NSPEC.....NUMBER OF DISTINCT SPECTRA PARAMETER
 SETS TO RAD IN
 11 - 20 IPLOT.....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 2: (I5)
 COLUMN
 1 - 5 LREN.....NUMBER OF LORENTZIAN IN MODEL OF DATA
 IF LREN = 0...OMIT CARDS 3 AND 4

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

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

C [==== CARD 5: (I10)
 C (COLUMN
 C (NSPEC TIMES 1 - 10 IFLAG.....FLAG FOR READING INCREMENTS

73/74 OPT=1 TRACE

FTN 4.6+452

```

C [
C [
C [
C [
C [
C [
C [
C [ (==
CARD 6: (4E10.4)
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 [ (
CARD 7: (5E10.4)
C [ ( INITIAL COLUMN
C [ ( VALUES OF 1 - 10 QS.....)QUADRUPOLE SPLITTING (CM/SEC)
C [ (
11 - 20 ETA.....)QUADRUPOLE ETA PARAMETER
C [ ( PARAMETERS 21 - 30 DELE.....)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 [ (
CARD 8: (5E10.4)
C [ (
COLUMN
C [ (
1 - 10 HYPERK.....KAPPA IN CALC OF A TENSOR
C [ (
11 - 20 PK.....)P*KAPPA/G(NUC)*BETA(NUC) IN KCE
C [ (
21 - 30 XYNN.....)
C [ (
31 - 40 XZNN.....) COVALENCY FACTORS
C [ (==
41 - 50 YZNN.....)
C [
C [ (==
CARD 9: (4E10.4)
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 [ (
CARD 10: (5E10.4)
C [ (
COLUMN
C [ ( INCREMENT 1 - 10 QS.....)QUADRUPOLE SPLITTING (CM/SEC)
C [ ( OF 11 - 20 ETA.....)QUADRUPOLE ETA PARAMETER
C [ ( CHANGE 21 - 30 DELE.....)ISOMER SHIFT (CM/SEC)
C [ ( OF 31 - 40 VJ2.....)RELAXATION PARAMETER (CM/SEC)
C [ ( PARAMETERS 41 - 50 WID.....)FULL WIDTH AT HALF MAXIMUM (CM/SEC)
C [ (
C [ (
CARD 11: (5E10.4)
C [ (
COLUMN
C [ (
1 - 10 HYPERK.....KAPPA IN CALC OF A TENSOR
C [ (
11 - 20 PK.....)P*KAPPA/G(NUC)*BETA(NUC) IN KCE
C [ (
21 - 30 XYNN.....)
C [ (
31 - 40 XZNN.....) COVALENCY FACTORS
C [ (==
41 - 50 YZNN.....)
C [ (==
C [
C [
C [
COMMON/ONE/PARA1(12)
COMMON/TWO/X(301),XLOW,XHIGH

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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/14*0/
READ 30,NSPEC,IPLOT,XLOW,XHIGH ,IPUNCH
30  FORMAT (2I10,2F10.5,I10)
    IF(XLOW.EQ.0.)  XLOW = -.5
    IF (XHIGH.EQ.0.)  XHIGH = .5
C
C  CALCULATE THE X AXIS
C
    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
40  FORMAT(1H1)
    ICOUNT = 0
    CHI = CHIOLD = 1.E15
    READ 100,IFLAG,((PARA(I,J),J=1,14),I=1,IFLAG)
100  FORMAT (I10,/, (4E10.4,/,5E10.4,/,5E10.4))
    IF(IFLAG.EQ.2) GO TO 150
C
C  SET UP PARAMETERS FOR NO VARIATION OF PARAMETERS
C
    ICOUNT = 1
    INDEX(1) = 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
210  CONTINUE
    DO 500 I1 = 1,ICOUNT
    DO 500 I2 = 1,ICOUNT
    IF (IFLAG.EQ.1) GO TO 250
C
C  SET UP PARAMETERS FOR FIRST TIME THRU VARIATION LOOPS
C
    I3 = INDEX(I2)
    PBEST = PINT = PARA(1,I3)
    DELTA = PARA(2,I3)
    PRINT 20
20  FORMAT (1H1)
    IF(I1.NE.1.OR.I2.NE.1) GO TO 270
C
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.

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

C
250 CALL PCALC
    CALL FERLX(EQ)
    IF(LREN.NE.0) CALL COMPAR(CHI)
C
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
    DO 260 I=1,301
    YDF(I) = YD(I)
    YCF(I) = YC(I)
260 CONTINUE
    YCFMIN = YCMIN
    YCFMAX = YCMAX
    YDFMIN = YDMIN
    YDFMAX = YDMAX
    IF (IFLAG.EQ.1) GO TO 500
C
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
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 YIELDED THE BEST CHI, IS
C NOT EQUAL TO THE VALUE BEFORE WE STARTED VARYING THE
C PARAMETER WE HAVE GONE THRU 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
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(12) = EQOLD
    PARA(1,I3) = PBEST
    CALL PCALC
500 CALL PLOTTER(CHI,LREN)

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      IF (IFLOT.EQ.0) GO TO 580
      CALL PLOTTYPE(IPL0T-1)
      CALL PLOTTYPE(0)
      YDIF = YCFMAX - YCFMIN
      YMAX = YCFMAX + .5*YDIF
      YMIN = YCFMIN - .5*YDIF
C
C   PLOT SPECTRA ON PLOTTER IF REQUESTED
C
      CALL PLOTDAT (X,YCF,301,YMIN,YMAX,X(1),X(301),0,8.,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 (  #  AXG = #,F12.7,#  AYG = #,F12.7,#  AZG = #,F12.7)
2020  FORMAT (  #  GX  = #,F12.7,#  GY  = #,F12.7,#  GZ  = #,F12.7)
2030  FORMAT (  #  QS  = #,F12.7,#  ETA = #,F12.7,#  IS  = #,F12.7)
2040  FORMAT (  #  VJ2 = #,F12.7,#  WID = #,F12.7,#  EQ  = #,F12.7)
      CALL PLOTEND
580  IF (IFUNCH.EQ.0) GO TO 600
      NPTS = 301
      PUNCH 590,YCFMIN,YCFMAX,XLOW,XHIGH,NPTS,(YCF(J),J=1,301)
590  FORMAT (2F10.4,2F10.5,I5,/, (8F10.4))
      KPUNCH = 5LPUNCH
      ENOFILF KPUNCH
600  CONTINUE
      END

```


73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE PCALC
COMMON/ONE/  PARA(12)
COMMON/EIGHT/ PARA(2,14)
DATA GNSN/1.18548 E-03/
HYPERK = PARA(1,10)
P = PARA(1,11) * GNSN/HYPERK
XYN = SQRT(PARA(1,12))
XZN = SQRT(PARA(1,13))
YZN = SQRT(PARA(1,14))
IF(YZN.EQ.0.)  YZN = XZN
A = PARA(1,1)
B = PARA(1,2)
C = PARA(1,3)
XKAP = PARA(1,4)
90  FORMAT (//, # A=#F9.6,2X,#B=#F9.6,2X,#C=#F9.6,2X,
1#XYN=#F9.6,2X,#XZN=#F9.6,2X,#YZN=#F9.6,2X,
1#HYPERK=#F9.6,2X,#P=#F9.6,2X,#PK=#F8.3)
R2 = SQRT(2.)
TWO7 = 2./7.
50  AA = A*A
BB = B*B
CC = C*C
AB = A*B
AC = A*C
BC = B*C
AC2 = A * C * 2.
C11 = EB * 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.
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.

C
C  TO DETERMINE A VALUE FOR P, THE FOLLOWING SHOULD BE NOTED.
C  IF
C    P = 2. * G(NUC) * BETA(NUC) * BETA * <R**3>
C    AND
C    NOTING THAT (FROM G. LANG)
C    P * HYPERK/(G(NUC)*BETA(NUC)) = 200KOE (APPROX)
C
C  FOR THE GROUND STATE HYPERFINE TENSOR,AND AX,AY,AZ WILL BE
C  IN CM/SEC.
C    AX = P*(4.*( C12I) - HYPERK * (-C11 + C22 + C33)
C    * + TWO7 * (-C11 + C22 - 2.*C33 - 3.*C13 + 3.*C23I))
C    AY = P*(4.*(-C13) - HYPERK * ( C11 + C22 + C33)
C    * + TWO7 * ( C11 - 2.*C22 + C33 + 3.*C12I - 3.*C23I))
C    AZ = P*(4.*( C23I) + HYPERK * ( C11 + C22 - C33)
C    * - TWO7 * (-2.*C11 + C22 - C33 - 3.*C12I - 3.*C13 ))
C
C  BEGIN FINAL PRINT OUT
C
C    PRINT 90,A,B,C,XYN,XZN,YZN,HYPERK,P,PARA(1,11)

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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) = 0.
RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE LORENTZ(LREN)
COMMON/TWO/X(301)
COMMON/FOUR/ YL(301),YLMIN,YLMAX,AREAL
DIMENSION HT(12),POS(12),GAM(12)
NP=301

```

```

C
C  INTRODUCE THE LORENTZIAN INFORMATION IF DESIRED
C
901  READ 5,LREN
5    FORMAT(I5)
    IF(LREN.EQ.0) RETURN
10   FORMAT(3E10.4)
    READ 10,BKG
    READ 10,(HT(I),GAM(I),POS(I),I=1,LREN)
    PRINT 905,LREN,BKG
905  FORMAT (1H1,///,*, FOR LORENTZIAN MODEL WITH #I2# PEAKS#
X    *, THE BACKGROUND IS #F10.5,///,T2,*,PEAK#,T14,*,HIGHT#,T26,
X    *,FULL-WIDTH AT HALF MAX#,T52,*,POSITION#,T69,*,AREA#,/)
    DO 910 I = 1,LREN
    AREA = GAM(I) * HT(I)*1.570796327
    PRINT 915,I,HT(I),GAM(I),POS(I),AREA
910  GAM(I) = (2.0/GAM(I))**2
915  FORMAT(1X,I4,5X,F10.6,11X,F10.8,9X,F10.8,5X,F10.5)
    AREAL = 0.
    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  YL(I) = BKG - F
    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

```

73/74 OPT=1 TRACE

FTN 4.6+452

C

```

SUBROUTINE FERLX(EQQ)
COMMON/ONE/PARA1(12)
COMMON/TWO/XD(301)
COMMON/THREE/YC(301),YCMIN,YCMAX
COMPLEX VAL(32), VEC(32,32)
DIMENSION WORK(2500)
DIMENSION WC(32)
COMPLEX Q21,Q22,Q21STR,Q22STR,EXPG1,EXPG2,EXPG3,EXPG4
COMPLEX H(32,32),P,VH(32),VM(32)
EQUIVALENCE (AXG,PARA1(1)),(AYG,PARA1(2)),(AZG,PARA1(3))
EQUIVALENCE (GX,PARA1(4)),(GY,PARA1(5)),(GZ,PARA1(6))
EQUIVALENCE (QS,PARA1(7)),(ETA,PARA1(8)),(DELE,PARA1(9))
EQUIVALENCE (VJ2,PARA1(10)),(WID,PARA1(11)),(EQ,PARA1(12))
RG = -0.5714
AXE = AXG * RG
AYE = AYG * RG
AZE = AZG * RG
NP=301

```

C

```

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

```

C

```

RADDEG = ATAN(1.)/45.
BETA = 0.
GAMA = 0.
ALFA = 0.
GAMA = GAMA*RADDEG
CSB = COS(BETA)
SNB = SIN(BETA)
CSA = COS(ALFA+ALFA)
SNA = SIN(ALFA+ALFA)
Q20 = 0.5 * (3.*CSB*CSB-1.0+ETA*SNB*SNB*CSA)
GAMA2 = GAMA+GAMA
EXPG1 = CMPLX(COS(GAMA),-SIN(GAMA))
EXPG2 = CMPLX(COS(GAMA2),-SIN(GAMA2))
EXPG3 = CONJG(EXPG1)
EXPG4 = CONJG(EXPG2)
Q21 = EXPG1*CMPLX(.5*ETA*SNB*SNA,.5*SNB*CSB*(3.-ETA*CSA))
Q21STR = EXPG3 * CMPLX(-.5*ETA*SNB*SNA,.5*SNB*CSB*(3.-ETA*CSA))
Q22 = EXPG2*CMPLX(-.5*ETA*SNA*CSB,.75*SNB*SNB+.25*ETA*CSA*
1 (1.+CSB*CSB))
Q22STR = EXPG4*CMPLX(.5*ETA*SNA*CSB,.75*SNB*SNB+.25*ETA*CSA*
1 (1.+CSB*CSB))
HZ = 0.
S = 0.
GAMMA = WID/2.
EQQ = EQ = (QS * 2.)/(SQRT(1.+(ETA*ETA/3.)))
PRINT 141, QS,ETA,DELE
141 FORMAT (1H0,*, QS = *,F12.7,*, ETA= *,F12.7,*, IS = *,F12.7)
PRINT 133,AZG,AYG,AXG
133 FORMAT (1X,*, AZ = *,F12.7,*, AY = *,F12.7,*, AX = *,F12.7)
PRINT 134, VJ2,WID,EQ
134 FORMAT (1X,*, VJ2= *,F12.7,*, WID= *,F12.7,*, EQ = *,F12.7)
PRINT 236,GX,GY,GZ
236 FORMAT (1X,*, GX = *,F12.7,*, GY = *,F12.7,*, GZ = *,F12.7)

```

73/74 OPT=1 TRACE

FTN 4.6+452

C
C PARAMETERS FOR ELECTRONIC SPIN MULTIPLICITIES ASSOCIATED WITH
C THE NUCLEAR LEVELS
C

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

C
C NUCLEAR SPIN MULTIPLICITY PARAMETERS
C

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

C
C QUADRUPCLE PARAMETER
C

RQG = EQ/(4.*RIG*(2.*RIG-1.))
RQG = 0.
RQE = EQ/(4.*RIE*(2.*RIE - 1.))
NMAT = 32
DO 511 I = 1,NP
511 YC(I) = 0.

C
C DEFINE EFFECTIVE RELAXATION RATES
C

WX = .5 * GX*GX*VJ2
WY = .5 * GY*GY*VJ2
WZ = .5 * GZ*GZ * VJ2
SS = .001
T = 1.
Z = 0.
K = 0
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

C
C.....
C

DO 2 ISGP = 1,NSZG
SZGP = FLOAT(ISGP)-RSG1
DO 2 ISEP = 1,NSZE
SZEP = FLOAT(ISEP) - RSE1

73/74 OPT=1 TRACE

FTN 4.6+452

```

DO 2 IIGP = 1,NIZG
ZIGP = FLOAT(IIGP)-RIG1
DO 2 IIEP = 1,NIZE
ZIEP = FLOAT(IIEP)-RIE1
L = L+1
H(K,L) = CMPLX(Z,Z)
C
C DIAGONAL TERMS OF H* .....
C
  NSG = ABS(SZG-SZGP)+SS
  NSE = ABS(SZE-SZEP)+SS
  NIG = ABS(ZIG-ZIGP)+SS
  NIE = ABS(ZIE-ZIEP)+SS
C
C SELECTION RULE .....
C
  IF(NSG.EQ.0.AND.NSE.EQ.0.AND.NIG.EQ.0.AND.NIE.EQ.0)
1    H(K,L) = CMPLX(Z,(AZG*SZG*ZIG-AZE*SZE*ZIE) +
2              Q20*(RQG*(3.*ZIG*ZIG-RIG*RIG1) -
3              RQE*(3.*ZIE*ZIE-RIE*RIE1))
4              + HZ*(SZG-SZE) )
  IF(NSG.EQ.0.AND.NSE.EQ.0.AND.NIG.EQ.0.AND.NIE.EQ.0) GO TO 400
C
C OFF DIAGONAL TERMS OF H* .....
C
  XP1 = 0.
  XM1 = 0.
  IF(NSE.NE.0.OR.NIE.NE.0) GO TO 1600
  SZGPL = SZG + 1.
  SZGMI = SZG - 1.
  ZIGPL = ZIG + 1.
  ZIGMI = ZIG - 1.
  NSP = ABS(SZGP - SZGPL) + SS
  NSM = ABS(SZGP - SZGMI) + SS
  NIP = ABS(ZIGP - ZIGPL) + SS
  NIM = ABS(ZIGP - ZIGMI) + SS
  IF(NSP.NE.0.OR.NIM.NE.0) GO TO 110
  XP1 = (RSG*RSG1-SZG*SZGPL)*(RIG*RIG1-ZIG*ZIGMI)
110  IF(NSM.NE.0.OR.NIP.NE.0) GO TO 120
  XM1 = (RSG*RSG1-SZG*SZGMI)*(RIG*RIG1-ZIG*ZIGPL)
120  FCT = (AXG+AYG)*(SQRT(XM1)+SQRT(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 125
      XP1 = (RSG*RSG1-SZG*SZGPL)*(RIG*RIG1-ZIG*ZIGPL)
125  IF(NSM.NE.0.OR.NIM.NE.0) GO TO 130
      XM1 = (RSG*RSG1-SZG*SZGMI)*(RIG*RIG1-ZIG*ZIGMI)
130  FCT = (AXG-AYG)*(SQRT(XM1)+SQRT(XP1))/4.
      H(K,L) = H(K,L) + CMPLX(Z,FCT)
C
C QUADRUPOLE GROUND STATE .....
C
  IF (NSG.NE.0) GO TO 1600
  XP1 = 0.
  XM1 = 0.
  IF (NIP.NE.0) GO TO 135

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      XP1 = (RIG*RIG1-ZIG*ZIGPL)
      FCT = (ZIGPL+ZIG)*SQRT(XP1)*RQG
      H(K,L) = H(K,L) + FCT*Q21
135  IF(NIM.NE.0) GO TO 140
      XM1 = (RIG*RIG1-ZIG*ZIGMI)
      FCT = (ZIGMI+ZIG) * SQRT(XM1)*RQG
      H(K,L) = H(K,L) + FCT*Q21STR
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)*(RIG1+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 = SQRT(XP1)*RQG
      FCT2 = SQRT(XM1)*RQG
      H(K,L) = H(K,L) + FCT2*Q22 + FCT1*Q22STR
1600 CONTINUE
C
C .....
C
      XP1 = 0.
      XM1 = 0.
      IF(NSG.NE.0.OR.NIG.NE.0) GO TO 2000
      SZEPL = SZE + 1.
      SZEMI = SZE - 1.
      ZIEPL = ZIE + 1.
      ZIEMI = ZIE - 1.
      NSP = ABS(SZEP-SZEPL) + SS
      NSM = ABS(SZEP-SZEMI) + SS
      NIP = ABS(ZIEP-ZIEPL) + SS
      NIM = ABS(ZIEP-ZIEMI) + SS
      IF(NSP.NE.0.OR.NIM.NE.0) GO TO 180
      XP1 = (RSE*RSE1-SZE*SZEPL)*(RIE*RIE1-ZIE*ZIEMI)
      XM1 = (RSE*RSE1-SZE*SZEPL)*(RIE*RIE1-ZIE*ZIEMI)
180  IF(NSM.NE.0.OR.NIP.NE.0) GO TO 190
      XM1 = (RSE*RSE1-SZE*SZEMI)*(RIE*RIE1-ZIE*ZIEPL)
190  FCT = -(AXE+AYE)*(SQRT(XM1)+SQRT(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*RSE1-SZE*SZEPL)*(RIE*RIE1-ZIE*ZIEPL)
195  IF(NSM.NE.0.OR.NIM.NE.0) GO TO 200
      XM1 = (RSE*RSE1-SZE*SZEMI)*(RIE*RIE1-ZIE*ZIEMI)
200  FCT = -(AXE-AYE)*(SQRT(XM1)+SQRT(XP1))/4.
      H(K,L) = H(K,L) + CMPLX(Z,FCT)
C
C QUADRUPOLE FOR EXCITED STATE .....
C
      IF(NSE.NE.0) GO TO 2000
      XP1 = 0.
      XM1 = 0.
      IF(NIP.NE.0) GO TO 225

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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)*(RIE-1.-ZIE)*(RIE+ZIEPL2)
250 IF(NIM2.NE.0) GO TO 260
XM1 = (RIE+ZIE)*(RIE1-ZIE)*(RIE-1.+ZIE)*(RIE-ZIEMI2)
260 FCT1 = -SQRT(XP1)*RQE
FCT2 = -SQRT(XM1)*RQE
H(K,L) = H(K,L) + FCT2*Q22 + FCT1*Q22STR
2000 CONTINUE
C
C.....
C
400 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 220
FCT = WZ*(2.*SZG*SZE-.5)-.5*(WX+WY)
H(K,L) = H(K,L) + CMPLX(FCT,Z)
GO TO 300
220 CONTINUE
FCT = 0.
IF(SZG*SZE.LT.0.0.AND.SZGP*SZEP.LT.0.0) FCT = .5*(WX-WY)
IF(SZG*SZE.GT.0.0.AND.SZGP*SZEP.GT.0.0) FCT = .5*(WX+WY)
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
H(J,J) = H(J,J) + P
4 IJOB = 2
CALL EIGCC (H,NMAT,NMAT,IJOB,VAL,VEC,NMAT,WORK,IER)
PRINT 3012, WORK(1),IER
3012 FORMAT(= PREFORMANCE CODE = ,F10.5,5X,=ERROR CODE = ,I5,/)
DO 460 J = 1,NMAT
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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

458  VEC(I,J) = VEC(I,J)/VNORM
460  CONTINUE
C
C   INCLUDE INTENSITIES
C
      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
      DO 100 IIG = 1,NIZG
      ZIG = FLOAT(IIG)-RIG1
      DO 100 IIE = 1,NIZE
      ZIE = FLOAT(IIE) - RIE1
      L = 0
      K = K+1
      WC(K) = 0.
      SS = .001
      NS = ABS(SZG-SZE) + SS
      DIF = ZIG - ZIE
      IF (DIF.LT.0.) SS = -.001
      NI = ZIG-ZIE +SS
      IF (NS.NE.0.OR.NI.NE.MD) GO TO 100
      WC(K) = FUN(ZIG,ZIE)
100  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)
13  VM(K) = VM(K) + WC(L) * CONJG(VEC(L,K))
      DO 40 I = 1,NP
      FP = 0.
C
C   ADD ISOMER SHIFT (DELE) INFORMATION
C
      P = CMPLX(Z,XD(I) - DELE)
      DO 41 K = 1,NMAT
      H(K,K) = VAL(K) - P
41  FP = FP + REAL(VM(K)*VIM(K)/H(K,K))
      YC(I) = YC(I) - FP
40  CONTINUE
47  CONTINUE
      CALL MINMAX(YC,YCMIN,YCMAX)
      RETURN
      END

```


73/74 OPT=1 TRACE

FTN 4.6+452

```

FUNCTION FUN(G,E)
SS = .001
ND = ABS(E-G) + SS
IF(ND.EQ.2) FUN = 0.
IF(ND.EQ.2) RETURN
IF(ND.EQ.0) FUN = SQRT(1./6.)
IF(ND.EQ.0) RETURN
IF(ND.EQ.1) FUN = SQRT(1./12.)
IF(ND.EQ.1.AND.E.GT.1.000.OR.E.LT.-1.000) FUN = .5
RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE COMPAR(CHI)
COMMON/THREE/YC(301),YCMIN,YCMAX
COMMON/FOUR/ YL(301),YLMIN,YLMAX,AREAL
COMMON/FIVE/ YD(301),YDMIN,YDMAX
C
C DO COMPARISON BETWEEN LORENTZIANS AND THEORY
C
   NP = 301
   CHI = 0.
   YLDIF = YLMAX - YLMIN
   AREAC = 0.
10  DO 10 I=1,NP
     AREAC = AREAC + ( YCMAX-YC(I))
   SCAL = AREAL/AREAC
   DO 960 I = 1,NP
     YC(I) =-SCAL*(YCMAX-YC(I))
     YD(I) = (YLMAX-YL(I))+ YC(I)
960  CHI = CHI + YD(I)**2
     CALL MINMAX(YD,YDMIN,YDMAX)
     PRINT 980,YDMIN,YDMAX,CHI
980  FORMAT (      * MINIMUM VALUE OF RESIDUAL = * F 10.7,
2/,* MAXIMUM VALUE OF RESIDUAL = * F10.7,/,
3  * FIT PARAMETER CHI = *7X,F10.4,///)
     CALL MINMAX (YC,YCMIN,YCMAX)
     YCMIN = YCMAX - YLDIF*1.2
RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE MOSSPLT (DAT,IV,IH,IDV,IDH,DATMIN,DATMAX)
  DIMENSION A(405) , DAT(1),IW(405) , IC(405) , SYMBOL(6)
  DIMENSION AXLAB(11)
  COMMON/TWO/ X(301),XMIN,XMAX
  DATA SYMBOL/'V','6','+',',','9','A','.'/
  DATA BLANK/' '
  XINC = (XMAX-XMIN)/10.
  AXLAB(1) = XMIN
  DO 10 I = 2,11
    AXLAB(I) = AXLAB(I-1) + XINC
  DELOAT = DATMAX - DATMIN
  XIV = FLOAT(IV)-0.0000001
  DO 2 I=1,IH,3
    IW(I) = TEMP = (DAT(I) -DATMIN)*XIV/(DELOAT) +1.
  2   IC(I) = (TEMP - IW(I)) * 5. + 1.
    IVP = IV + 1
    DO 4 J = 1,IVP
      K = IVF - J + 1
      DO 3 I = 1,IH,3
        A(I) = BLANK
        IF(MOD(K,IDV).EQ.1) A(I) = SYMBOL(6)
        IF(MOD(I,IDH*3).EQ.1) A(I) = SYMBOL(6)
        IT = IC(I)
        IF(IW(I).EQ.K) A(I) = SYMBOL(IT)
      3   CONTINUE
    PRINT 100,(A(L),L=1,IH,3)
  4   CONTINUE
100  FORMAT(4X,131A1)
    PRINT 1090,AXLAB
1090 FORMAT(2X,11(F5.2,5X))
    RETURN
  END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE PLOTTER (CHI,LREN)
  COMMON/ONE/PARA1(12)
  COMMON/SIX/ 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)
10  FORMAT (1H1,/,# AXG = #F12.7#   AYG = #F12.7#   AZG = #F12.7,
A   /, # GX = #,F12.7,#   GY = #,F12.7,#   GZ = #,F12.7,
1   /, # QS = #,F12.7,#   ETA = #,F12.7,#   IS = #,F12.7,
2   /, # VJ2 = #,F12.7,#   WID = #,F12.7,#   EQ = #,F12.7)
  CALL MOSSPLT(YCF,30,301,5,10,YCFMIN,YCFMAX)
  IF(LREN.EQ.0) RETURN
  PRINT 980,YDFMIN,YDFMAX,CHI
980  FORMAT (///, # MINIMUM VALUE OF RESIDUAL = #F10.7,
1     # MAXIMUM VALUE OF RESIDUAL = #F10.7,
2     # CHI = #F10.4)
  CALL MOSSPLT (YDF,20,301,20,10,YDFMIN,YDFMAX)
  RETURN
  END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      SUBROUTINE PLOTDAT(X,Y,NX,YMIN,YMAX,XMIN,XMAX,NDAT,
      1XSIZE,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 PLOTDAT WITH A CALL
C TO PLOTTYPE. PLOTTYPE 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 AVAILABEL 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 I 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(1),Y(1)
C THE SIZE ROUTINE FIXES THE BOUNDS OF THE PLOT. THE CALLING
C STRING IS:
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   XSIZ = AMAX1(15.,XSIZE+5.)
C   YSIZ = AMAX1(10.,YSIZE+4.)
C   CALL SIZE(XSIZ,YSIZ)
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 FACTR 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

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73/74 OPT=1 TRACE

FTN 4.6+452

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C          LEFT AS A MARGIN ON THE LEFT OF PLOTTING AREA AS DEFINED
C          BY THE SIZE COMMAND.
C      YBIAS - A BIAS FACTOR IN INCHES. THIS AMOUNT WILL BE LEFT AS
C          A MARGIN AT THE BOTTOM OF THE PLOTTING AREA AS DEFINED
C          BY THE SIZE ROUTINE.
C      XLOW - THE LOWEST VALUE IN YOUR UNITS OF THE X-AXIS.
C      YLOW - THE LOWEST VALUE IN YOUR UNITS OF THE Y-AXIS.
C
C      XSCAL = XSIZE/(XMAX-XMIN)
C      YSCAL = YSIZE/(YMAX-YMIN)
C
C      CALL SCALE(XSIZE/(XMAX-XMIN),YSIZE/(YMAX-YMIN),XBIAS,YBIAS,
C      1XMIN,YMIN)
C THE AXIS ROUTINE HAS PARAMETERS
C      CALL AXISL(XLOW,XHIGH,XORGIN,YLOW,YHIGH,YORGIN,XTIC,YTIC,LXTIC,LYTIC,
C      1LINTX,LINTY,XUNIT,YUNIT,CSIZE,XSCAL,YSICAL)
C WHERE
C      XLOW - THE LOWEST VALUE IN YOUR UNITS OF X AXIS.
C      XHIGH - THE HIGHEST VALUE IN YOUR UNITS OF X-AXIS.
C      XORGIN - THE CROSSING POINT ALONG THE X-AXIS OF THE Y-AXIS.
C      YLOW - THE LOWEST VALUE IN YOUR UNITS OF THE Y-AXIS.
C      YHIGH - THE HIGHEST VALUE IN YOUR UNITS OF THE Y-AXIS.
C      YORGIN - THE CROSSING POINT ALONG THE Y-AXIS OF THE X-AXIS.
C      XTIC - THE DISTANCE IN YOUR UNITS BETWEEN MAJOR TIC MARKS
C      YTIC - THE DISTANCE IN YOUR UNITS BETWEEN MAJOR TIC MARKS
C          ALONG THE Y-AXIS.
C      LXTIC - NUMBER OF MINOR TIC MARKS BETWEEN EACH MAJOR TIC MARK ON
C          X AXIS
C      LYTIC - THE NUMBER OF MINOR TIC MARKS BETWEEN EACH MAJOR TIC
C          MARK ON THE Y AXIS
C      LINTX - LABELING FREQUENCY ON X AXIS
C      LINTY - LABELING FREQUENCY ON Y AXIS
C      XUNIT - SCALING VALUE FOR LABELS ON X AXIS
C      YUNIT - SCALING FACTOR FOR LABELS ON Y AXIS
C      CSIZE - SIZE OF CHARACTERS IN THE LABELS
C      XSCAL - AS DEFINED ABOVE
C      YSCAL - AS DEFINED ABOVE
C
C      NOTE*****
C      AXISL IS NOT THE ROUTINE DEFINED IN COMLOT R THE ARAND
C      MANUAL. ALL BUT THE LAST TWO PARAMETERS ARE EXACTLY FROM
C      AXISL AS DEFINED IN THE ARAND MANUAL. THIS VERSION WAS
C      WRITTEN BY SWM SINCE THE LABELING IN THE CURRENT CYBER VERSION
C      (29 MAR 77) WAS NOT ACCEPTABLE TO THE STANDARDS REQUESTED BY
C      HHW. THE LOG AXES ARE NOT AVAILABLE IN THIS VERSION, AND
C
C      SCALING FACTORS MUST BE ENTERED IN THE PARAMETER STRING.
C*****
C
C TO DETERMINE THE VALUES FOR XTIC AND YTIC A ROUTINE CALLED AMARK IS
C USED
C
C      CALL TMARK(DIF,AMARK,N)
C
C      WHERE
C      DIF - THE DIFFERENCE IN USERS UNITS FOR THE LENGTH OF THE AXIS

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73/74 OPT=1 TRACE

FTN 4.6+452

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C   AMARK - THE DISTANCE IN USERS UNITS BETWEEN MAJOR TIC MARKS.
C           THIS WILL BE EITHER 1.,2.,OR 5. TIMES A POWER OF TEN.
C           AND IS DETERMINED BY AMARK.
C   N - THE MINIMUM NUMBER OF PARTS TO DIVIDE THE AXIS UP INTO.
C           THE AXIS WILL BE DEVIDED UP INTO BETWEEN N AND 2*N NUMBER OF
C           EQUAL PARTS.
C
C   CALL TMARK(XMAX-XMIN,XTIC,10)
C   CALL TMARK(YMAX-YMIN,YTIC,5)
C
C   YHI = YMIN + (YMAX-YMIN)*.8
C   CALL AXISL(XMIN,XMAX,0.,YMIN,YHI,YMIN,XTIC,YTIC,4,4,4,-1,1.,
C   11.,.12,XSCAL,YSCAL)
C
C   MARK=IABS(NOAT)
C   THE ROUTINE TO PLOT IS
C   CALL PLOT(X,Y,IPEN,MARK)
C   WHERE
C   X - X COORDINATE IN YOUR UNITS OR POINT TO PLOT TO.
C   Y - Y COORDINATE IN YOUR UNITS OF FOINT TO PLOT TO.
C   IPEN - 0 MOVE TO POINT WITH PEN UP, 1 MOVE TO POINT WITH PEN DOWN
C   MARK - AND INTEGER FROM 0 28 FO MARK TO DRAW AT THE POINT
C   CALL VECTORS
C   CALL PLOT(X,Y,G,MARK)
C   IF(NOAT.LT.0) CALL POINTS
C   DO 20 I=2,NX
C   CALL PLOT(X(I),Y(I),1,MARK)
C 20 CONTINUE
C   CALL ALPHAS
C   RETURN
C   END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE TMARK(DIF,AMARK,N)
C
C   THIS SUBROUTINE WILL DETERMINE THE PROPER INTERVAL FOR SPACING
C   TIC MARKS ALONG AN AXIS BY BREAKING THE AXIS UP INTO BETWEEN N AND
C   2*N PARTS. THE TIC MARKS WILL BE LOCATED AT POINTS WHICH ARE EITHER
C   1., 2., OR 5. TIMES SOME POWER OF 10 USERS UNITS APART. THIS
C   NUMBER WILL BE RETURNED AS AMARK. DIF IS THE LENGTH OF THE TOTAL
C   AXIS IN USERS UNITS.
C
C   DIMENSION JTIC(9)
C   DATA JTIC/1,2,2,2,5,5,5,5,5/
C   AMARK = ABS(DIF)/FLOAT(N)
C   ILOG = XLOG = ALOG10(AMARK)
C   IF(XLOG.LT.0.) ILOG = ILOG - 1
C   IMARK = AMARK * (10.**(-ILOG))
C   IF (IMARK .GE.10) IMARK = 9
C   IF (IMARK.LT.1) IMARK = 1
C   AMARK = FLOAT(JTIC(IMARK))*(10.**ILOG)
C   RETURN
C   END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE AXISL (XMIN,XMAX,XORG,YMIN,YMAX,YORG,XTIC,YTIC,
1LXTIC,LYTIC,LINTX,LINTY,XUNIT,YUNIT,CSIZE,XSCALE,YSCALE)
CALL AXIS (XMIN,XMAX,XORG,YMIN,YMAX,YORG,XTIC,YTIC,LXTIC,LYTIC)
XOFF = CSIZE/(2.*XSCALE)
YOFF = CSIZE*2./YSCALE
IF (LINTX) 100,300,200
200 XT = XTIC
XEND = XMAX
DO 290 J=1,2
NTIC = ABS((XEND-XORG)/XT)
IF (NTIC.LT.LINTX) GO TO 280
DO 280 I = LINTX,NTIC,LINTX
X = XORG + XT*FLOAT(I)
CALL LABELS(X/XUNIT,ARRAY,NPRINT)
260 CALL SYMBOL(X-NPRINT*XOFF,YORG-YOFF,0.,CSIZE,NPRINT,ARRAY)
280 XT = -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 ,500,600
600 YT = YTIC
YEND = YMAX
DO 590 J=1,2
NTIC = ABS((YEND-YORG)/YT)
IF (NTIC.LT.LINTY) GO TO 580
DO 580 I = LINTY,NTIC,LINTY
Y = YORG + FLOAT(I) * YT
CALL LABELS(Y/YUNIT,ARRAY,NPRINT)
XMARK = XORG - FLOAT(NPRINT + 2) * XOFF
560 CALL SYMBOL(XMARK,Y-YOFF,0.,CSIZE,NPRINT,ARRAY)
580 YT = -YT
YEND = YMIN
590 CONTINUE
400 CALL LABELS(YMIN/YUNIT,ARRAY,NPRINT)
XMARK = XORG - FLOAT(NPRINT + 2) * XOFF
CALL SYMBOL (XMARK,YMIN,0.,CSIZE,NPRINT,ARRAY)
CALL LABELS(YMAX/YUNIT,ARRAY,NPRINT)
XMARK = XORG - FLOAT(NPRINT + 2) * XOFF
CALL SYMBOL (XMARK,YMAX-2.*YOFF,0.,CSIZE,NPRINT,ARRAY)
500 RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE LABELS (VAL,ARRAY,NPRINT)
AVAL = ABS(VAL)
IF(AVAL.GT.999.99.OR. AVAL .LT. .01) GO TO 100
N = 6
ILOG = XLOG = ALOG10(AVAL)
M = 4 - ILOG
IF(XLOG.LT.0.) M = 5
IF(VAL .LT.0.) N = 7
NPRINT = N - M + 2
NCHAR = N
ENCODE (6,50,FMT) N,M
50  FORMAT (1(F#,I1,1,1,1,1,1,1))
40  JJ = IFIX((AVAL+.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(E8.2)
    GO TO 200
130  NCHAR = NPRINT = 7
    FMT = 6H(E7.2)
200  ENCODE (NCHAR,FMT,ARRAY) VAL
    RETURN
20  ARRAY = 1H0
    NCHAR = NPRINT = 1
    RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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.,0.,0,0)
  CALL PLOT (11.,0.,1,0)
  CALL PLOT (11.,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 (5.50,8.2,1,28)
  CALL PLOT(9.75,8.2,1,28)
  CALL SYMBOL (4.3,8.55,0,...12,20,CUTOUT)
  RETURN
END

```

APPENDIX V
Program MULTEPR

73/74 OPT=1 TRACE

FTN 4.6+452

PROGRAM MULTPR(INPUT,OUTPUT,TAPE61=OUTPUT,TAPE10)

```

C
C THIS PROGRAM COMPUTES THE POLYCRYSTALLINE ABSORPTION PATTERN
C FOR THE FOLLOWING SYSTEM:
C   SPIN.....S = 1/2
C   G-TENSOR.....GX,GY,GZ
C   RF = MICROWAVE FREQUENCY (IN GHZ)
C   GAM = WIDTH AT HALF-MAXIMUM OF LORENTZ LINE
C   RF = MICROWAVE FREQUENCY (IN GHZ)
C   GAM = WIDTH AT HALF-MAXIMUM OF LORENTZ LINE
C         (LORENTZ LINESHAPE ASSUMED)
C   HL = LOWER FIELD LIMIT (IN KOE)
C   HU = UPPER FIELD LIMIT (IN KOE)
C   NSPEC = NUMBER OF SPECTRA TO BE SIMULATED
C   NB = NUMBER OF THETA POINTS
C   NC = NUMBER OF PSI POINTS
C   NPOINTS = NUMBER OF DATA POINTS FOR SPECTRUM PLOT
C   XLENGTH = LENGTH OF X AXIS IN INCHES (DEFAULT = 10.)
C   YLENGTH = LENGTH OF Y AXIS IN INCHES (DEFAULT = 6.)
C   CHARSZ = HIGHT OF CHARACTERS ON PLOT (DEFAULT = .12)
C   SP = ABSORPTION SPECTRUM
C   DSP = DERIVATIVE SPECTRUM
C   DSFTOT = TOTAL DERIVATIVE SPECTRUM(ACD MIXTURE)
C   NCOMP = NUMBER OF COMPONENTS FOR A GIVEN SPECTRA
C   NSET = NUMBER OF SETS OF WEIGHTING FACTORS TO BE READ IN
C   WT = WEIGHTING FACTOR GIVEN TO EACH COMPONENT OF SPECTRA
C   IPLOT = DEFINES PLOTTER TO BE USED. IF IPLOT = 0, CALCOMP
C           PLOTTER IS USED. IF IPLOT = 3, THE GERBER PLOTTER IS USED.
C
C THIS PROGRAM ALLOWS ADD MIXTURES OF SPECTRA TO BE CALCULATED. IF
C MORE THAN ONE SPECTRA IS TO BE MIXED, NCOMP IS SET TO THE NUMBER OF
C COMPONENT SPECTRA TO BE ADDED TOGETHER. EACH COMPONENT IS WEIGHTED
C BY THE WEIGHTING FACTOR WT. THERE WILL BE ONE WEIGHTING FACTOR FOR EACH
C COMPONENT. WT(1) WILL BE ASSOCIATED WITH THE FIRST COMPONENT,
C WT(2) WITH THE SECOND, ETC.
C
C ONE SPECTRA IS DEFINED AS HAVING NSPEC COMPONENTS. THUS IF THREE
C ONE COMPONENT SPECTRA ARE TO BE CALCULATED, NSPEC = 3, AND NCOMP = 1
C FOR EACH SPECTRA. IF TWO THREE COMPONENT SPECTRA ARE TO BE CALCULATED
C NSPEC = 2, AND NCOMP = 3 FOR EACH SPECTRA. IF NCOMP IS GREATER
C THAN 1 (A MULTI COMPONENT SPECTRA), WIEGHTING FACTORS ARE READ IN
C AND THE NCOMP COMPONENTS OF THE SPECTRA ARE WEIGHTED AND ADDED
C TOGETHER. SEVERAL DIFFERENT MIXING RATIOS OF ONE SPECTRA CAN THEN
C BE CALCULATED.
C
C IF NB OR NC ARE TO BE DETERMINED INTERNALLY (SET TO ZERO ON INPUT)
C THE FOLLOWING FORMULA IS USED:
C
C   NB(OR NC) = 6. * (CONST * RF * ((1./AMIN1(G)) - (1./AMAX1(G)))+GAM)/GAM
C   WHERE G = GX,GY,GZ
C
C
C
C
C EULER ANGLES FROM RUTHERFORD.....PHYSICAL ROTATIONS SO THERE ARE
C NEGATIVE ANGLES IN EACH OF RUTHERFORDS SIMPLE ROTATOIN

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73/74 OPT=1 TRACE

FTN 4.6+452

C MATRICIES

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

C RUTHERFORD CALLS HIS FIRST ROTATION ANGLE PHI. HENCE
 C PHI(RUTHERFORD) = PSI(HHW)

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

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

C INPUT PARAMETERS

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

C COLUMN

C 1 - 10 NSPEC
 C 11 - 20 XLENGTH (DEFAULT = 10.)
 C 21 - 30 YLENGTH (DEFAULT = 6.)
 C 31 - 40 CHARSZ (DEFAULT = .12)
 C 41 - 50 IPLOT

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

C COLUMN

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

C CARD 3 (4E10.4,2I5)

C COLUMN

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

C CARD 4 (I5)

C COLUMN

C 1 - 5 NSET

C CARD 5 (10F8.0)

C COLUMN

C 1 - 8 WT(1)
 C 9 - 16 WT(2)
 C 17 - 24 WT(3)
 C 25 - 32 WT(4)

73/74 OPT=1 TRACE

FTN 4.6+452

```

C -----
C                                     +
C                                     +
C -----
C      ! CALCULATE THE TOTAL SPECTRA FROM ADD MIXTURES !
C      ! AND PLOT IT                                     !
C -----
C                                     +
C                                     +
C -----
C      ! INCREMENT ISET AND CHECK IF ISET > NSET         !>>>>NO>>>>
C -----
C                                     +
C                                     +
C      + YES
C -----
C(A)>: INCREMENT ISPEC AND CHECK IF ISPEC > NSPEC         !>>>>>>NO>>>>>>
C -----
C                                     +
C                                     +
C      + YES
C -----
C      ! END !
C -----
C
C      DIMENSION SP(512),X(512),DSP(512,10),DSPTOT(512),WT(10)
C      DIMENSION ARRAY(9),TITLE(3)
C      REAL IX,IY,IZ
C      DATA XOFF/3./,YOFF/3./
C      DATA (TITLE =21HMAGNETIC FIELD IN KOE)
C      PI = 4. * ATAN(1.)
C      CONST = 6.62554 E-18/.92731 E-17
C
C      CONST = PLANCKS CONST/BETA      IN UNITS OF KOE SEC
C
C      READ IN NUMBER OF SPECTRA TO BE SIMULATED AND NUMBER OF DATA POINTS
C
C      WRITE (61,25)
C      25 FORMAT (#1#)
C      READ 10,NSPEC,XLENGTH,YLENGTH,CHARSZ,IPLLOT
C      10 FORMAT(I10,3F10.5,I10)
C
C      ASSIGN DEFAULT VALUES FOR PLOT PARAMETERS
C
C      IF (XLENGTH.EQ.0.)      XLENGTH = 10.
C      IF (YLENGTH.EQ.0.)      YLENGTH = 6.
C      IF (CHARSZ.EQ.0.)      CHARSZ = .12
C      CALL PLOTTYPE (IPLLOT)
C      CALL PLCTLUN(10)
C      CALL SIZE (1.5*XLENGTH + XOFF,1.5*YLENGTH + YOFF)
C
C      LOOP ON NSPEC
C
C      DO 1010 ISPEC=1,NSPEC
C
C      READ IN CARD TYPE 2 AND ASSIGN DEFAULT VALUES
C
C      READ 15,RF,HL,HU,NPOINTS,NCOMP
C      15 FORMAT (3E10.4,2I5)
C      IF (NPOINTS.EQ.0)      NPOINTS = 201

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73/74 OPT=1 TRACE

FTN 4.6+452

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      IF (NCOMP.EQ.0) NCOMP = 1
C
C   USE HL, HU, AND NPOINTS TO CALCULATE THE X-AXIS
C
      HDIF = HU - HL
      HMID = HL + HDIF/2.
      DELH = HDIF/FLOAT(NPOINTS - 1)
      X(1) = HL
      DO 110 I=2,NPOINTS
110   X(I) = X(I-1) + DELH
C
C   LOOP ON NCOMP THEN
C   READ IN PARAMETERS CHARACTERIZING THE ICOMP COMPONENT OF A SPECTRA
C   CARD TYPE 3
C
320   DO 2000 ICOMP = 1,NCOMP
      READ 20,GX,GY,GZ,GAM,NB,NC
20    FORMAT (4E10.4,2I5)
C
C   CALCULATE THE FEWEST NUMBER OF POINTS NECESSARY FOR A
C   GOOD SPECTRA AS DESCRIBED EARLIER AND ASSIGN IT TO NB OR NC
C   AS PRE DEFAULT REQUIREMENTS
C
      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
C
C   PRINT OUT SPECTRA PARAMETERS ON LINE PRINTER SO THE USER KNOWS
C   WHAT HE REQUESTED.
C
      PRINT 21, ISPEC, ICOMP, GX, GY, GZ, NB, NC, RF, GAM, HL, HU, NPOINTS
21    FORMAT (# SPECTRA SIMULATED ... #I5/# COMPONENT ... #I5
E/,#0GX #,T10,#=#E12.5/# GY#,T10,
A #=#E12.5/# GZ#,T10,#=#E12.5/# NB(THETA)#,T10,#=#
B I5/# NC(PSI)#,T10,#=#I5/# RF#,T10,#=#E12.5/# GAM#,T10,#=#E12.5/# H
CL#,T10,#=#E12.5/# HU#,T10,#=#E12.5/# NPOINTS#,T10,#=#I5/#0#/#0#)
C
C   ZERO OUT ABSORPTION SPECTRA
C
      DO 108 I=1,NPOINTS
108   SP(I)=0.
C
C   BEGIN LOOPS ON THETA (NB) AND PSI (NC) TO SAMPLE POSSIBLE
C   EFFECTIVE G-VALUES
C
      XA = XB = XC = 0.
      IF (NB.NE.1) XB=(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

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73/74 OPT=1 TRACE

FTN 4.6+452

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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+
1CB2*SC2))/(2.*GEFF2)
  HI = SQRT(HI)*SB
  A = 0.
  B = B + .XB
C
C SUM UP LORENTZ ABSORPTION PEAKS AT RESONANCE FIELDS
C
  DO 115 I=1,NPOINTS
    SP(I) = SP(I) +FL(X(I),HO,HI,GAM)
115  CONTINUE
800  CONTINUE
    B = 0.
    C = C + XC
900  CONTINUE
C
C NORMALIZE THE AREA UNDER THE CURVE TO ONE USING THE
C TRAPEZIOD RULE
C
  CALL NORMAL (SP,NPOINTS)
C
C CALCULATE DERIVATIVE OF SPECTRUM
C
  DELH2 = 2. * DELH
  NPNTS1 = NPOINTS - 1
  DO 99 I=2,NPNTS1
    DSP(I,ICOMP) = (SP(I+1) - SP(I-1))/DELH2
99  CONTINUE
    DSP(1,ICOMP) = DSP(2,ICOMP)
    DSP(NPOINTS,ICOMP) = DSP(NPNTS1,ICOMP)
C
C
C PLOT SPECTRUM
  CALL BOX(XOFF,YOFF,XLENGTH,YLENGTH)
C
C AUTOSCALE THE DATA
C
195  SPMIN = SPMAX = 0.
    DO 201 I=1,NPOINTS
201  IF (SP(I).GT.SPMAX) SPMAX=SP(I)
C
  SPDIF = SPMAX - SPMIN

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73/74 OPT=1 TRACE

FTN 4.6+452

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SPMIN = SPMIN - SPDIF/2.
SPMAX = SPMAX + SPDIF/2.
SPDIF = SPDIF * 2.
XSCAL = XLENGTH/HOIF
YSCAL = YLENGTH/SPDIF
CALL SCALE (XSCAL,YSCAL,XOFF,YOFF,HL,SPMIN)
C
C DRAW THE AXIS
C
CALL AXIS (HL,HU,HL,SPMIN,SPMAX,SPMIN,HOIF/10.,0.,1,G)
C
C LABEL THE X-AXIS
C
CALL AXIS (HL,HU,HU,SPMIN,SPMAX,SPMAX,HOIF/10.,0.,1,G)
XXOFF = 3. * CHARSZ/XSCAL
YXOFF = 2. * CHARSZ/YSCAL
ENCODE (6,202,ARRAY) HL
202 FORMAT (F6.3)
CALL SYMBOL (HL-XXOFF,SPMIN-YXOFF,0.,CHARSZ,6,ARRAY)
ENCODE (6,202,ARRAY) HU
CALL SYMBOL (HU-XXOFF,SPMIN-YXOFF,0.,CHARSZ,6,ARRAY)
CALL SYMBOL (HMID-3.5*XXOFF,SPMIN-2.*YXOFF,0.,CHARSZ,21,
1 TITLE)
C
C PLOT THE DATA
C
HF = HL
CALL PLOT (HF,SP(1),0,0)
DO 203 I=1,NPOINTS
C
C IN ORDER FOR THE PLOT TO LOOK NICE AND KEEP COSTS DOWN. THE
C SPECTRA IS PLOTTED AS A DOTTED LINE.
C
IPEN = MOD(I,3)
CALL PLOT (HF,SP(I),IPEN,0)
203 HF = HF + DELH
ENCODE (55,204,ARRAY) GX,GY,GZ
204 FORMAT (#GX = #F10.6,5X,#GY = #F10.6,5X,#GZ = #F10.6)
CALL SYMBOL (HL+2.*XXOFF,SPMAX-YXOFF,0.,CHARSZ,55,ARRAY)
ENCODE (69,205,ARRAY) RF,GAM
205 FORMAT (#MICROWAVE FREQUENCY(GHZ) = #F10.6,5X,#LINEWIDTH(KOE) = #
1,F10.6)
CALL SYMBOL (HL+2.*XXOFF,SPMAX-2.5*YXOFF,0.,CHARSZ,69,ARRAY)
ENCODE (55,206,ARRAY) ICCMP,NB,NC
206 FORMAT (#COMPONENT #I5,5X,#NB(TH) = #I5,5X,#NC(PSI) = #I5)
CALL SYMBOL (HL+2.*XXOFF,SPMAX-4.*YXOFF,0.,CHARSZ,55,ARRAY)
C
C PLOT DSP SPECTRUM
C
DSPMIN=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 = YLENGTH/DSPDEL

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73/74 OPT=1 TRACE

FTN 4.6+452

```

CALL SCALE (XSCAL,YSCAL,XOFF,YOFF,HL,DSPMIN)
HF = HL
CALL PLOT (HL,DSP(1,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.EQ.1) GO TO 1010
READ 400,NSET
400  FORMAT(I5)
DO 1000 ISET = 1,NSET
READ 410,WT
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
C PLOT DSPTOT SPECTRUM
C
  DSPMIN=DSPMAX=0.
  DO 39 I=1,NPOINTS
  IF (DSPTOT(I).LT.DSPMIN) DSPMIN = DSPTOT(I)
39  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
C DRAW THE AXIS
C
  CALL AXIS (HL,HU,HL,DSPMIN,DSPMAX,DSPMIN,HDIF/10.,0.,1,0)
C
C LABEL THE X-AXIS
C
  CALL AXIS (HL,HU,HU,DSPMIN,DSPMAX,DSPMAX,HDIF/10.,0.,1,0)
  XXOFF = 3. * CHARSZ/XSCAL
  YXOFF = 2. * CHARSZ/YSCAL
  ENCODE (6,202,ARRAY) HL
  CALL SYMBOL (HL-XXOFF,DSPMIN-YXOFF,0.,CHARSZ,6,ARRAY)
  ENCODE (6,202,ARRAY) HU
  CALL SYMBOL (HU-XXOFF,DSPMIN-YXOFF,0.,CHARSZ,6,ARRAY)
  CALL SYMBOL(HMID-3.5*XXOFF,DSPMIN-2.*YXOFF,0.,CHARSZ,21,
1  TITLE)
C
C THE FOLLOWING CODE PUTS THE WEIGHTING FACTORS ON THE
C TOP OF THE COMPOSITE SPECTRA. SINCE THERE ARE
C UP TO 13 WEIGHTING FACTORS AND ROOM FOR ONLY FIVE
C ACROSS, THE FOLLOWING CODE CHECKS FOR THE
C NUMBER OF LINES NECESSARY AND CALLS THAT JJ. THE NUMBER
C OF WEIGHTING FACTORS ON ONE LINS IS GIVEN BY NTIME.

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73/74 OPT=1 TRACE

FTN 4.6+452

```

C
  JJ = FLOAT(NCOMP)/5. + .9
  DO 510 J = 1,JJ
    NTIME = MIN0(5,NCOMP-5*(J-1))
    NCHAR = 16 * NTIME
    J1 = (J-1) * 5
    NCOUNT = J1 + NTIME
    J1 = J1 + 1
C
C  CODE UP ONE OR TWO LINES, WHERE NCOUNT IS THE NUMBER PER LINE
C
    ENCODE(NCHAR,502,ARRAY)  NTIME,(I,WT(I),I=J1,NCOUNT)
502  FORMAT(=,I2,=,F5.3)
510  CALL SYMBOL (HMID-2.667*NTIME*XXOFF,DSPMAX-J*YXOFF,0.,CHARSZ,
      1  NCHAR,ARRAY)
C
C  PLOT DATA NOW
C
    HF = HL
    CALL PLOT (HL,DSPTOT(1),0,0)
    DO 41 I=1,NPOINTS
      CALL PLOT (HF,DSPTOT(I),1,0)
41  HF = HF + DELH
    CALL PLOTEND
1000  CONTINUE
1010  CONTINUE
    END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE BOX(X,Y,XL,YL)
  DIMENSION CUTOUT(2)
  DATA CUTOUT/20HCUT 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 PLOT ( 0.,0.,0,0)
  CALL PLOT (11.,0.,1,0)
  CALL PLOT (11.,8.5,1,0)
  CALL PLOT ( 0.,8.5,1,0)
  CALL PLOT ( 0.,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.,.12,20,CUTOUT)
  CALL VECTORS
  RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

FUNCTION FL(X,W,HI,G)
FL = (FI)/(4.*(((X-W)/G)**2) + 1.)
RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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

```

APPENDIX VI
Program MOSSFIT

73/74 OPT=1 TRACE

FTN 4.6+452

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

```

C
C MOSSFIT USES THE BELL LABS VERSION OF NLLSQ MODIFIED TO RUN
C ON A CYBER 73 COMPUTER. THE USER IS REFERED TO THE WRITE-UP
C ON THE ORIGINAL PROGRAM BEFORE MAKING ANY CHANGES IN THE
C REQUESTED OUTPUT OR OPTIONS.
C
C INPUT PARAMETERS:
C     B = THE ARRAY CONTAINING THE INPUT PARAMETERS FOR THE FIT
C     KITER = THE NUMBER OF ITERATIONS TO USE IN FITTING
C           IF KITER > 99, THE PROGRAM STOPS.
C     NPAIR = THE NUMBER OF PAIRS OF PEAKS TO BE FIT.
C     NSING = THE NUMBER OF SINGLE PEAKS TO BE FIT
C     NPLT = FLAG FOR PLOTTING OF DATA AND FITTED CURVE.
C           IF NPLT IS POSITIVE NONZERO, THE PLOT WILL BE DONE ON THE
C           CALCOMP PLOTTER. IF ZERO, NO PLOT.
C           IF NPLT IS NEGATIVE THE PLOT IS DONE ON THE GERBER.
C     NCAL = FITTING FLAG FOR CALIBRATIONS IF NCAL NE 0
C           CALIBRATION CONSTANTS ARE CALCULATED
C     TITLE = A TITLE FOR THE RUN (FURNISHED BY MOSSRED).
C     YMAX,YMIN,NPTS,AND NOEL ARE SCALING INFORMATION USED IN
C           PLOTTING
C     VELC AND CG ARE THE CALIBRATION CONSTANTS FOR THE SPECTRA
C     X, AND Y ARE THE DATA ARRAYS
C
C THIS PROGRAM FITS A MOSSBAUER SPECTRA OF INTENSITY (RELATIVE)
C AS A FUNCTION OF CHANNEL NUMBER. THE MODEL USED IS LORENTZIAN.
C THE PEAKS ARE EITHER SPECIFIED AS SINGLE PEAKS, CHARACTERIZED
C BY AN INTENSITY OR HEIGHT, A FULL WIDTH AT HALF MAXIMUM, AND A
C POSITION; OR AS PAIRS OF PEAKS, CHARACTERIZED BY A HEIGHT, FULL WIDTH
C AT HALF MAXIMUM, POSITION OF THE FIRST PEAK, POSITION OF THE SECOND
C PEAK, AND A RATIO, WHERE RATIO = HT1/HT2. THE HEIGHT AND FULL
C WIDTH AT HALF MAX FOR THE SECOND PEAK IS CALCULATED FROM THE
C HEIGHT AND WIDTH OF THE FIRST PEAK, ASSUMING THE AREA UNDER BOTH
C PEAKS IS THE SAME.  THUS:
C
C           HT2 = HT1/RATIO
C           GAM2 = GAM1 * RATIO
C
C WHERE
C           HT1 AND HT2 ARE THE HEIGHTS OF THE FIRST AND SECOND
C           PEAKS RESPECTIVELY. GAM1 AND GAM2 ARE THE FULL WIDTH
C           AT HALF MAXIMUM FOR THE FIRST AND SECOND PEAKS
C           RESPECTIVELY.
C
C THUS WE CAN SEE THAT  $HT2 * GAM2 = HT1 * GAM1 * RATIO/RATIO$ 
C                       $= HT1 * GAM1$ 
C
C AND HENCE THE PEAKS HAVE THE SAME AREA. THE UNITS OF HEIGHT ARE
C RELATIVE INTENSITY UNITS, THE OTHER PARAMETERS ARE IN UNITS
C OF CHANNELS. THE HEIGHT OF THE PEAKS IS THE INTENSITY
C UNITS DOWN FROM A BASELINE OR BACKGROUND WHICH MUST ALSO
C BE SPECIFIED. IF RATIO IS SET TO ZERO FOR THE PAIRS OF PEAKS
C THE DEFAULT VALUE OF -1 IS USED. THAT IS, THE RATIO IS HELD
C FIXED AT 1. HOLDING VALUES CONSTANT WILL BE DISCUSSED LATER.
C
C
C TO DETERMINE THE CALIBRATION CONSTANTS FOR AN IRON FOIL CALIBRATION
C SET NCAL NON-ZERO AND SPECIFY THE PEAKS AS PEAK PAIRS WITH SPLITTINGS
C GOING FROM LARGEST TO SMALLEST. IF 3 PEAK PAIRS ARE PRESENT, THE

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73/74 OPT=1 TRACE

FTN 4.6+452

C PROGRAM ASSUMES THAT THE 10.657 MM/SEC PAIR IS FIRST PAIR SPECIFIED
 C THE 6.167 MM/SEC IS THE SECOND, AND THE 1.677 MM/SEC PAIR IS THIRD.
 C IN DETERMINING THE CG AND VELC, THE RELATIVE INTENSITIES OF THE PEAK
 C PAIRS ARE USED AS WEIGHTING FACTORS.

C THE INPUT CARD TYPES READ CONTAIN THE FOLLOWING:

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

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

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

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

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

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

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

C CARD 8:
 C YMAX, YMIN, CG, VELC, NPTS, NOEL
 C (4F10.5, 2I5)
 C THIS CARD IS PROVIDED BY MOSSRED

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

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

C EXAMPLE 1: FOR MODEL WITH 3 PAIRS OF PEAKS, THE FOLLOWING
 C CARD TYPES ARE NEEDED:

73/74 OPT=1 TRACE

FTN 4.6+452

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C          1,2,3,3,3,7,8,9-A,1(WITH KITER >99)
C
C  EXAMPLE 2:  FOR MODEL WITH 4 SINGLE PEAKS, THE FOLLOWING
C              CARD TYPES ARE NEEDED:
C              1,2,5,5,5,5,7,8,9-A,1(WITH KITER > 99)
C
C  EXAMPLE 3:  FOR MODEL WITH 2 PAIRS OF PEAKS AND 3 SINGLE PEAKS,
C              THE FOLLOWING CARD TYPES ARE NEEDED:
C              1,2,3,3,5,5,5,7,8,9-A,1(WITH KITER > 99)
C
C  IF MORE THAN ONE DECK IS TO BE FIT IN THE SAME RUN, THE DECK
C  STRUCTURE REQUIRED FOR THE SECOND RUN SIMPLY FOLLOWS THE FIRST.
C
C  OUTPUT
C
C  THE PROGRAM GENERATES PUNCH, LINE PRINTER AND PLOT OUTPUT
C  AS FOLLOWS:
C
C  PUNCH:
C          CARD 1:  BKG
C                  (F10.5)
C          CARD 2-N:  HIEGHT, HALF-WIDTH, AND POSITION
C                   (3F10.5)
C                   THERE WILL BE ONE CARD FOR EACH PEAK
C
C  LINE PRINTER:
C          INTERMEDIATE OUTPUT AS SPECIFIED BY NARRAY(5)
C          FINAL OUTPUT AS SPECIFIED BY NARRAY(6), EXCEPT THAT
C          THE DATA AND CALCULATED MODEL ARE NOT PRINTED DUE TO A
C          GO TO STATEMENT IN THE SUBROUTINE NLLSQ.  THE REMAINING
C          PRINT CUT GIVES THE TITLE, FINAL FITTED PARAMETERS, AND
C          THE INITIAL ESTIMATES FOR ALL PEAKS.
C
C  PLOTTER:
C          PLOT OUTPUT CONTAINS THE INITIAL DATA,
C          THE FINAL MODEL, THE PARAMETERS FOR EACH PEAK, THE
C          BACKGROUND, AND VERTICAL LINES DRAWN TO INDICATE
C          THE HEIGHT AND POSITION OF EACH PEAK.
C          IF CALIBRATION INFO IS AVAILABLE, THE CG AND VELC
C          ARE PRINTED ON THE PLOT, A VELOCITY AXIS IS DRAWN
C          THE PARAMETERS GAMMA AND POSITION ARE GIVEN IN UNITS
C          OF MM/SEC.
C          A SEPARATE PLOT OF THE RESIDUALS IS ALSO PLOTTED.
C
C  ONE OPTION OF THIS PROGRAM ALLOWS THE USER TO HOLD ANY PARAMETER
C  OR PARAMETERS FIXED FOR THE RUN.  THIS IS DONE BY GIVING THE
C  PARAMETER A NEGATIVE VALUE.  THE NEGATIVE VALUE SETS A FLAG TO
C  HOLD THE PARAMETER FIXED AND THE ABSOLUTE VALUE OF THE TERM IS
C  THEN SUBSTITUTED FOR IT.
C
C  ADDITIONAL ARRAYS USED IN THE PROGRAM:
C      BB = THE INITIAL PARAMETERS FOR PRINTING
C      A  = THE PEAK PARAMETERS AS SINGLE PEAKS ONLY
C          FOR USE IN PLOTTING
C      RES = RESIDUAL ARRAY FROM NLLSQ
C      NARRAY, ARRAY ARE ARRAY ARE PARAMETERS FOR NLLSQ AND
C          EXPLAINED IN THE WRITE UP FOR THE SUBROUTINE

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73/74 OPT=1 TRACE

FTN 4.6+452

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C      IB = THE INDEX(ES) OF THE PARAMETERS TO BE HELD CONSTANT
C
C      DECK STRUCTURE:
C      THE FOLLOWING CONTROL CARDS MUST BE USED FOR THE CYBER VERSION
C      IF NO PLOTTING IS TO BE DONE, THE LABEL CARD SHOULD BE OMITTED.
C
C      USER,50350,ABCD.  (REPLACE ABCD WITH APPROPRIATE USER CODE.)
C      CHARGE,725160,A.
C      SETTL,500.
C      LABEL,TAPE10,VSN=13014,LB=KU,F=S,FO=W,PW=ABCD.
C      (USE WHAT EVER IS APPROPRIATE FOR VSN = , AND PW = )
C      REWIND,TAPE10.
C      GET,FITBIN.
C      ATTACH,COMPLLOT/UN=LIBRARY.
C      LDSET,L19=COMPLLOT.
C      FITBIN.
C      REWIND,TAPE10.
C      7/8/9
C      .
C      .
C      DATA DECK AS PREVIOUSLY DESCRIBED
C      .
C      .
C      6/7/8/9
C
C      THIS PRESUPPOSES THAT THE BINARY DECK FOR THIS PROGRAM IS
C      ON THE PERMANENT FILE FITBIN.  TO CREATE THAT FILE USE:
C
C      USER,50350,ABCD.  (REPLACE ABCD WITH APPROPRIATE USER CODE.)
C      CHARGE,725160,A.
C      SETTL,500.
C      FTN,8=FITBIN.
C      SAVE,FITBIN.
C      7/8/9
C      .
C      .
C      FORTRAN DECK OF MOSSFIT
C      .
C      .
C      6/7/8/9
C
C      IF THE BINARY FILE DOES NOT EXIST BUT A BINARY DECK DOES, THE
C      BINARY FILE MAY BE CREATED BY THE FOLLOWING:
C
C      USER,50350,ABCD.  (REPLACE ABCD WITH APPROPRIATE USER CODE.)
C      CHARGE,725160,A.
C      SETTL,500.
C      COPYBF,INPUT,FITBIN.
C      7/8/9
C      .
C      .
C      BINARY DECK OF MOSSFIT
C      .
C      .
C      6/7/9
C      6/7/8/9
C

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73/74 OPT=1 TRACE

FTN 4.6+452

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C
C TO RUN THE PLOT FROM THE TAPE CREATED BY MOSSFIT, THE FOLLOWING
C OS-3 DECK MUST BE RUN. SEE COMP CENTER NEWSLETTER VOL XI, NO. 4, PAGE 5.
C (NOTE THAT IN THE FOLLOWING THE SYMBOL( REPRESENTS THE OS-3 CONTROL PUNCH)
C
C      (JOB,MT1,72516C,      ,SAVE FOR WICKMAN
C      (EQUIP,1=MT,13014,AT 800,R PW=ABCD
C      (TIME=200
C      (MFBLKS=400
C      (REWIND,1
C      (EQUIP,2=PLOT
C      (LABEL,2/WICKMAN
C      (COPY,I=1,O=2,P=0
C      (REWIND,1
C      (LOGOFF
C
C
C
C *****
C IF THE GERBER PLOTTER IS USED,MODIFY THE DECK STRUCTURE
C ACCORDING TO THE CYBER COMLOT MANUAL
C *****
C
C      DIMENSION X(512),Y(512),B(45)
C      DIMENSION A(90)
C      DIMENSION BB(45)
C      DIMENSION TITLE(10)
C      DIMENSION NARRAY(8),ARRAY(8),IB(45),RES(512),FMT(10)
C      COMMON/DATA5/NPAIR,NSING
C      NPLOT = 0
C      PID2 = 2. * ATAN(1.)
C
C READ IN FITTING INFORMATION
C
C      READ 10,KITER,NPAIR,NSING,NPLT,NCAL
C      FORMAT (5I5)
C      IF (KITER.GT.99) GO TO 901
C      NTOT=1
C
C READ IN BACKGROUND
C
C      READ 30,B(1)
C      FORMAT (5F10.5)
C
C READ IN PARAMETERS FOR PAIRS OF PEAKS IN NPAIR > 0
C
C      IF (NPAIR) 40,60
C      NTOT=NTOT+5*NPAIR
C      DO 50 I=2,NTOT,5
C      NSUB=I+4
C      READ 30,(B(J),J=I,NSUB)
C
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

```


73/74 OPT=1 TRACE

FTN 4.6+452

```

C      IF (3(NSUB).EQ.0.) B(NSUB) = -1.
53    CONTINUE
C
C    READ IN PRARMETERS 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(I)=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.
      ENCODE (89,110,FMT) TITLE
110   FORMAT (2(1H0,80H#,10A8,#)2)
      CALL NLLSQ (Y(NOEL),X(NOEL),B,RES(NOEL),NARRAY,ARRAY,IB,FMT)
      IF (NCAL.NE.0) CALL CALIB(B,NPAIR,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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      PRINT 107,TITLE
137  FORMAT (1H1,134(1H*),//,28X,10A8
      1,/,44X,FINAL (AND INITIAL) FITTING PARAMETERS FROM NLLSQ
      2,/,1X,134(1H*))
      PUNCH 15,TITLE
      IF (VELC.NE.0.) PRINT 108,VELC,CG
108  FORMAT (//,5X,VELC = ,G14.7,MM/SEC/CH,5X,CG = ,G14.7,CH)
      PRINT 120,B(1),BB(1)
120  FORMAT (//,X0 BACKGROUND = ,G14.7,(,G14.7,)#)
      PUNCH 200,B(1)
      A(1) = B(1)
      KK=2
      IF (NPAIR) 130,150
130  PRINT 140,NPAIR
140  FORMAT (X0 FOR THE #I2# PAIRS OF PEAKS THE PARAMETERS#
      1# ARE: ,/,1H0,13X,HIGHT#25X,HALF-WIDTH#25X,POSITION#
      225X,HT1/HT2 ,/)
      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 290,(B(J),BB(J),J=I,NSUB),B(I+4),BB(I+4)
      PUNCH 200,B(I),B(I+1),B(I+2)
      R = B(I+4)
      AREA = PID2*B(I+1) * B(I)
      RR = BB(I+4)
      A(KK) = B(I)/R $ A(KK+1) = B(I+1)*R $ A(KK+2) = B(I+3)
      BB(I) = BB(I)/RR $ BB(I+1) = BB(I+1)*RR
      PUNCH 200,A(KK),A(KK+1),A(KK+2)
      PRINT 295,A(KK),BB(I),A(KK+1),BB(I+1),A(KK+2),BB(I+3),AREA
      KK = KK+3
145  CONTINUE
150  IF (NSING) 160,190
160  PRINT 170,NSING
170  FORMAT (X0 FOR THE #I2# SINGLE PEAKS, THE #
      1#PARAMETERS ARE: ,/,1H0,13X,HIGHT#,25X,HALF-WIDTH#,
      225X,POSITION#,/)
      NTOT=NTOT+3*NSING
      DO 180 I=NL,NTOT,3
      NSUB=I+2
      AREA = PID2*B(I+1) * B(I)
      PRINT 295,(B(J),BB(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 NLLSQPT (Y,A,KK,NPLT,NDEL,NPTS,YMAX,YMIN,RES,TITLE,CG,VELC,
      1NPLT)
      GO TO 1
901  CONTINUE
      IF (MOD(NPLT,4).NE.0) CALL PLOTEND
      ENDFILE 10

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      ENDFILE 10
      STOP
200  FORMAT (3F10.5)
290  FORMAT(4(1X,G14.7,± (±,G14.7,±) ±))
295  FORMAT(3(1X,G14.7,± (±,G14.7,±) ±),± PEAK AREA = ±G16.9)
      END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      SUBROUTINE CALIB(B,NPAIR,CG,VELC)
      DIMENSION B(45),V(3)
C
C  THIS SUBROUTINE CALCULATES THE CALIBRATION CONSTANTA  FOR AN IRON
C  FOIL SPECTRUM.
      DATA V/1.677,6.167,10.657/
      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)*(B(J+2) + SPLIT/2.)
      HTTOT = HTTOT + B(J)
10    J=J+4
      VELC = VELC/HTTOT
      CG = CG/HTTOT
      RETURN
      END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE MODEL(F,Y,X,RRR,I,JP)
COMMON/BLK1/P(45),PARTIAL(45),RE,N,M,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
RGAMSQ = RGAM * RGAM
RGAM2SQ = RGAM2 * RGAM2
DIS1 = X(I) - P1
DIS2 = X(I) - P2
DIS1SQ = DIS1*DIS1
DIS2SQ = DIS2*DIS2
DENOM1 = DIS1SQ * RGAMSQ + 1.
DENOM2 = DIS2SQ * RGAM2SQ + 1.
D1SQ = DENOM1 * DENOM1
D2SQ = DENOM2 * DENOM2
PARTIAL(K) = -(1./DENOM1 + 1./(R*DENOM2))
PARTIAL(K+1) = -(HT*DIS1SQ*RGAM*RGAMSQ/D1SQ +
1 HT*DIS2SQ*RGAM2*RGAM2SQ/D2SQ)
PARTIAL(K+2) = -2.*HT*DIS1*RGAMSQ/D1SQ
PARTIAL(K+3) = -2.*HT2*DIS2*RGAM2SQ/D2SQ
PARTIAL(K+4) = (HT/(R*R*DENOM2))*(1.-2.*DIS2SQ*RGAM2SQ/DENOM2)
F = F - HT/DENOM1 - HT2/DENOM2
704 CONTINUE
705 CONTINUE
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=(Z*G1)+1.0
FN1=U1**2
D1=P(K2)/FN1
PARTIAL(K2)=(-1.0/U1)
PARTIAL(K3)=((-8.0*D1*G1)/(P(K3)**3))
PARTIAL(K4)=(-2.0*D1*W1*Z)
F=F+(F(K2)*PARTIAL(K2))
720 CONTINUE
707 RE=Y(I)-F
RRR(I)=RE
RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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
COMMON/BLK1/B(45),P(45),RE,N,M,K
COMMON/BLK2/A(90,45),SA(45),K2,IK,NPMAX
COMMON/BLK3/BS(45),DB(45),G(45),K3
COMMON/BLK4/AL,DELTA,E,FF,GAMCR,T,TAU,ZETA,PHI,SE,PHICR
COMMON/BLK5/IB(45),IP
DIMENSION Y(1),X(1,1),RES(1)
DIMENSION BB(45),IBB(45)
DIMENSION FMT(45)
DIMENSION NARRAY(8),ARRAY(9)
DIMENSION CONST(8),SCONST(8)
EQUIVALENCE(CONST,AL)
DATA (SCONST=0.1,1.1E-5,5.0E-5,4.0,45.0,2.0,0.001,1.0E-31)
NPMAX=45
N=NARRAY(1)
M=NARRAY(2)
K=NARRAY(3)
K2=K
K3=K
IP=NARRAY(4)
INTP=NARRAY(5)
IFF=NARRAY(6)
IK=NARRAY(7)
IF(NARRAY(8).EQ.(-1)) NARRAY(8)=KITER
KITER=NARRAY(8)
C   WHICH OF THE CONSTANTS HAVE BEEN DETERMINED BY USER
DO 5 J=1,8
IF(ARRAY(J).LE.0.)GO TO 4
CONST(J)=ARRAY(J)
GO TO 5
4  CONST(J)=SCONST(J)
5  CONTINUE
IF(KITER.LE.0) KITER=30
IF(IK.LE.0) IK=6
26 IF(IFF.EQ.(-1))GO TO 100
WRITE(IK,2090)
WRITE(IK,FMT)
WRITE(IK,2001)N,K,M,DELTA,E,FF,GAMCR,T,TAU,ZETA,AL
100 DO 120 J=1,K
BS(J)=BB(J)
B(J)=BE(J)
120 CONTINUE
DO 121 J=1,IP
121 IB(J)=IBB(J)
CALL SUMSQ(PHI,Y,X,RES)
LJ=0
130 IF(LJ.GE.KITER)GO TO 404
LJ=LJ+1
C   BEGIN LJTH ITERATION
CALL NEWA(Y,X,RES)
1311 IF(AL.LT..1E-67) GO TO 131

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      AL=AL/10.
131  CALL SCAL
      PHIOLD=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)*G(J)/(SA(J)*SA(J))
      DD=DD+DB(J)*DB(J)*SA(J)*SA(J)
152  DG=DG+DB(J)*G(J)
      XL=SQRT(DD)
      IF(DD*GG.GT.0.)GO TO 160
155  GAMMA=0.
      GO TO 170
160  CGAM=DG/SQRT(DD*GG)
      GAMMA=0.
      IF(CGAM*CGAM.GE.1.)GO TO 170
      WS=SQRT(1.-CGAM*CGAM)
      GAMMA=57.2957795*ATAN2(WS,CGAM)
170  CALL SUMSQ(PHI,Y,X,RES)
171  IF(PHI.LE.PHIOLD)GO TO 175
      IF(GAMMA-GAMCR)300,300,180
175  DO 176 J=1,K
176  BS(J)=B(J)
      IF (GAMMA.LT.90.) GO TO 190
C    GAMMA LAMBDA TEST
178  IF(AL-1.)190,403,403
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
200  IF(INTP.EQ.0)GO TO 130
      WRITE(IK,2000)
      WRITE(IK,2002)LJ,PHI,AL,(B(J),J=1,K)
      WRITE(IK,2003)GAMMA,XL,(CB(J),J=1,K)
      IF(INTP.EQ.1)GO TO 130
      CALL NEWA(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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

207 IF(IATP.EQ.2)GO TO 210
    WRITE(IK,2004)
    CALL PRINT1
210 CALL SCAL
    WRITE(IK,2006)
    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
        OB(J)=OB(J)/2.
320  B(J)=BS(J)+OB(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,2090)
    WRITE(IK,FMT)
    WRITE(IK,2010)
    GO TO 405
402 IF(IFP.EQ.(-1))GO TO 4025
    WRITE(IK,2090)
    WRITE(IK,FMT)
    WRITE(IK,2011)
4025 IF(IFP.NE.(-1).AND.PHIOLD.LT.PHI)WRITE(IK,2092)
    IF(PHICLD.GE.PHI)GO TO 4029
    PHI=PHIOLD
    DO 4027 J=1,K
4027 B(J)=BS(J)
4029 IF(IFP.EQ.(-1)) GO TO 600
    GO TO 405
403 IF(IFP.EQ.(-1))GO TO 600
    WRITE(IK,2090)
    WRITE(IK,FMT)
    WRITE(IK,2012)
    GO TO 405
404 WRITE(IK,2013)
    NARRAY(8)=-1
    IF(IFP.EQ.(-1))GO TO 600
    WRITE(IK,FMT)
405 DO 406 J=1,K
    BS(J)=B(J)
406  BB(J)=B(J)
    WRITE(IK,2002)LJ,PHI,AL,(B(J),J=1,K)
    WRITE(IK,2003)GAMMA,XL,(OB(J),J=1,K)
    CALL NEWA(Y,X,RES)

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      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,RE
461  CONTINUE
C     ONE PARAMETER SUPPORT PLANE COMPUTATIONS
      FNKW=N-K+IP
      IF(FNKW.LE.0.)GO TO 589
      FKW=K-IP
      SE=SQRT(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
462  CONTINUE
464  STE=SA(I)*SE
      HJTD=SQRT(FF*FKW)*STE
      OPL=BS(I)-STE*T
      OPU=BS(I)+STE*T
      SPL=BS(I)-HJTD
      SPU=BS(I)+HJTD
      WRITE(IK,2041)I,STE,OPL,OPU,SPL,SPU
      GO TO 470
469  WRITE(IK,2042)I
470  CONTINUE
      IF (IFF.EQ.1) GO TO 602

```


73/74 OPT=1 TRACE

FTN 4.6+452

```

C      NONLINEAR CONFIDENCE REGION CALCULATIONS
      WS=FKW/FNKM
      PHICR=PHI*(1.+WS*FF)
      WRITE(IK,2049)PHICR
      CALL CONFRG(Y,X,RES)
      IF(IFP.GE.0)WRITE(IK,2090)
      RETURN
589  WRITE(IK,2060)
590  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  B9(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,I,J)
      IF(IFP.GE.0)WRITE(IK,2090)
      RETURN
2000  FORMAT(100HXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
1XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX/1H0)
2001  FORMAT(21HNO OF DATA POINTS IS,I4,22H NO OF PARAMETERS IS,I3,3X
1,30HNO OF INDEPENDENT VARIABLES IS,I3/7HDELTA=,E15.8,5H E=,E15.
28,6H 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(1X/19HNO OF ITERATIONS =I3/6H0PHI =,E15.8,4X,8HLAMBDA =,
1E15.8/11H0PARAMETERS/(1X,7E17.8/))
2003  FORMAT(8H0GAMMA =,E15.8,4X,14HLENGTH OF DB =,E15.8/21H0DB CORRECTI
1ON VECTOR/(1X,7E17.8/))
2004  FORMAT(1X/12H0PTP INVERSE)
2006  FORMAT(1X/25H0CORRELATION COEFFICIENTS)
2010  FORMAT(28H0CONVERGENCE BY EPSILON TEST)
2011  FORMAT(34H0CONVERGENCE BY GAMMA EPSILON TEST)
2012  FORMAT(33H0CONVERGENCE BY GAMMA LAMBDA TEST)
2013  FORMAT(10H1FORCE OFF)
2022  FORMAT(1X/11H0PTP MATRIX)
2023  FORMAT(1X/29H0PTP CORRELATION COEFFICIENTS)
2024  FORMAT(1X/12H0PTP INVERSE)
2025  FORMAT(1X/35H0PARAMETER CORRELATION COEFFICIENTS)
2030  FORMAT(1X/1H0,6X,11H OBSERVED,11X,9HPREDICTED,10X,8HRESIDUAL/1X)
2031  FORMAT(1X,I3,3X,2(E15.8,4X),E15.8)
2040  FORMAT(1X/1H0,12X,4H STD,18X,15HONE - PARAMETER,22X,13HSUPPORT PLA
1NE/2X,4HPARA,7X,5HERROR,13X,5HLOWER,13X,5HUPPER,13X,5HLOWER,13X,5H
2UPPER)
2041  FORMAT(2X,I3,5E18.8)
2042  FORMAT(2X,I3,5X,23HPARAMETER HELD CONSTANT)
2049  FORMAT(1X/29H0 NONLINEAR CONFIDENCE LIMITS/15H0PHI CRITICAL =E15.8
1/6H0 PARA,6X,8H LOWER B,8X,10H LOWER PHI,10X,8H UPPER B,8X,10H UPP
2ER PHI)
2060  FORMAT(57H0OUTPUT IS ABBREVIATED DUE TO MATHEMATICAL CONSIDERATION
1S)
2090  FORMAT(1H1)
2092  FORMAT(50H0CORRECTION VECTOR FOR LAST ITERATION WAS NOT USED)
      END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE NEWA(Y,X,RES)
C  NEWA - CALCULATES PTP MATRIX, A, AND GRADIENT VECTOR, G.
  DIMENSION Y(1),X(1,1),RES(1)
  COMMON/BLK1/B(45),P(45),RE,N,M,K
  COMMON/BLK2/A(90,45),SA(45),K2,IK,NPMAX
  COMMON/BLK3/BS(45),DB(45),G(45),K3
  COMMON/BLK4/AL,DELTA,E,FF,GAMCR,T,TAU,ZETA,PHI,SE,PHICR
  COMMON/BLK5/IB(45),IP
  DO 1 J=1,K
    G(J)=0.
    P(J)=0.
    DO 1 I=1,K
      A(J,I)=0.
1    DO 50 II=1,N
C    LOOK FOR PARTIALS
      J=2
      CALL MODEL(F,Y,X,RES,II,J)
      RD=RE
      DO 30 JJ=1,K
C      CHECK FOR OMITTED PARAMETERS
      IF(IP.GT.0)GO TO 25
10    GO TO(20,30,20),J
C    COMPUTE PARTIALS IF NECESSARY
20    AB=B(JJ)
      BDEL=AE*DELTA
      IF(BDEL.EQ.0.)BDEL=DELTA
      B(JJ)=AB+BDEL
      J=1
      CALL MODEL(FDEL,Y,X,RES,II,J)
      RE=RD
      P(JJ)=(FDEL-F)/BDEL
      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)
      DO 40 I=1,K
      DO 40 J=1,K
40    A(I,J)=A(I,J)+P(I)*P(J)
50    CONTINUE
      DO 55 I=1,K
      DO 55 J=1,K
55    A(J,I)=A(I,J)
C    A(I,I)=1.0 FOR OMITTED PARAMETER I
      IF(IP.EQ.0)RETURN
      DO 60 I=1,IP
      DO 60 J=1,K
60    IF(J.EQ.IB(I))A(J,J)=1.
      RETURN
  END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

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/BLK2/A(90,45),SA(45),K2,IK,NPMAX
COMMON/BLK4/AL,DELTA,E,FF,GAMCR,T,TAU,ZETA,PHI,SE,PHICR
DIMENSION P(45),Q(45),B(45),C(45)
INTEGER P,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=K,N
IF(ABS(A(I,J))-ABS(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).EQ.K) GO TO 80
DO 70 J=1,N
L=P(K)
Z=A(L,J)
A(L,J)=A(K,J)
70  A(K,J)=Z
C   EXCHANGE OF COLUMN
80  IF(Q(K).EQ.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.EQ.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 I=1,N
DO 10 J=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 (P(K).EQ.K) GO TO 170
DO 180 I=1,N
L=P(K)
Z=A(I,L)
A(I,L)=A(I,K)

```

```

180 A(I,K)=Z
170 IF(Q(K).EQ.K)GO TO 155
    DO 150 J=1,N
    L=Q(K)
    Z=A(L,J)
    A(L,J)=A(K,J)
150 A(K,J)=Z
155 CONTINUE
    RETURN
40 WRITE(IK,45)P(K),Q(K),PIVOT
45 FORMAT(20H0SINGULAR MATRIX I=,I3,4H J=,I3,8H PIVOT=E16.8/)
    MSING=2
    RETURN
    END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

C SUBROUTINE SUMSQ(PHI,Y,X,RES)
  COMPUTES SUM OF SQUARES
  DIMENSION Y(1), X(1,1),RES(1)
  COMMON/BLK1/B(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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

C 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,I
  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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE SOLVE
C SOLVES (PTP)(DB)=(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,IK,NPMAX
COMMON/BLK3/BS(45),DB(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+NPMAX
  DO 9 J=1,K
    9 A(I,J)=A(II,J)
  10 A(I,I)=1.+AL
  20 CALL GJR(MS)
  GO TO (25,100),MS
  25 DO 40 I=1,K
    DB(I)=0.
    IF(SA(I).LE.0.)GO TO 40
    DO 30 J=1,K
      IF(SA(J).LE.0.)GO TO 30
      DB(I)=A(I,J)*G(J)/SA(J) +DB(I)
    30 CONTINUE
    DB(I)=DB(I)/SA(I)
  40 CONTINUE
  RETURN
100 AL=AL*10.
  L=L+1
  IF(L.GE.6)STOP
  GO TO 1
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE ETEST(ML)
COMMON/BLK1/B(45),P(45),RE,N,M,K
COMMON/BLK3/BS(45),DB(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)))
  IF (W.GE.EPS) GO TO 30
20 CONTINUE
  GO TO 40
30 ML=2
40 RETURN
END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

C      SUBROUTINE PRINT1
      PRINTS A K BY K SINGLE PRECISION MATRIX
      COMMON/BLK2/A(90,45),SA(45),K2,IK,NPMAK
      K=K2
      L=1
5      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/8H0COLUMNS,I4,9H THROUGH,I4)
106    FORMAT(1X,7E17.8)
      END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

C      SUBROUTINE PRINT2
      PRINTS A K BY K CORRELATION COEFFICIENT MATRIX
      COMMON/BLK2/A(90,45),SA(45),K2,IK,NPMAK
      L=1
      K=K2
5      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/8H0COLUMNS,I4,9H THROUGH,I4)
107    FORMAT(1X,13F9.4)
      END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE CONFRG(Y,X,RES)
C   CONFRG - NON LINEAR CONFIDENCE REGION CALCULATIONS
COMMON/BLK1/B(45),P(45),RE,N,M,K
COMMON/BLK2/A(90,45),SA(45),K2,IK,NPMAX
COMMON/BLK3/BS(45),DB(45),G(45),K3
COMMON/BLK4/AL,DELTA,E,FF,GAMCR,T,TAU,ZETA,PHI,SE,PHICR
COMMON/BLK5/IS(45),IP
DO 500 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.IS(I)) GO TO 506
504  CONTINUE
    GO TO 509
506  WRITE(IK,2042) J
    GO TO 580
509  DDS=-1.
510  D=DDS
    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=D/2.
    IF(ABS(D).LE..001) GO TO 570
    B(J)=BS(J)+D*DJ
    CALL SUMSQ(PPH,Y,X,RES)
    IF(PPH-PHICR) 540,540,520
530  D=D+DDS
    IF(ABS(D).GE.5.0) GO TO 570
    B(J)=BS(J)+D*DJ
    CALL SUMSQ(PPH,Y,X,RES)
    IF(PPH.LT.PHICR) GO TO 530
540  Q=1.-D
    XK1=PHI/D+PH/Q-PPH/(D*Q)
    XK2=-PHI*(1.+D)/D-PH*D/Q+PPH/(D*Q)
    XK3=PHI-PHICR
    BC=(-XK2+SQRT(XK2**2-4.*XK1*XK3))/(2.*XK1)
    IF(DDS.GT.0.) GO TO 550
    B(J)=BS(J)-BC*DJ
    BL=B(J)
    CALL SUMSQ(PL,Y,X,RES)
548  DDS=1.
    GO TO 510
550  B(J)=BS(J)+BC*DJ
    BU=B(J)
    CALL SUMSQ(PU,Y,X,RES)
    GO TO 576
570  IF(DDS.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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

      GO TO 580
576  IF (NOLONE.0) GO TO 578
      WRITE(IK,2052)J,BL,PL,BU,PU
      GO TO 580
C    OMITTING LOWER LIMITS
578  WRITE(IK,2053)J,BU,PU
580  B(J)=BS(J)
2042 FORMAT(2X,I3,5X,23HPARAMETER HELD CONSTANT)
2052 FORMAT(2X,I3,4E18.8)
2055 FORMAT(2X,I3,2E18.8,11H NOT FOUND)
2053 FORMAT(2X,I3,11H NOT FOUND,25X,2E18.8)
2056 FORMAT(2X,I3,18X,11H NOT FOUND)
      RETURN
      END

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE BOX(X,Y)
  DIMENSION CUTOUT(2)
  DATA CUTOUT/20HCUT 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 (11.,0.,1,0)
  CALL PLOT (11.,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 (5.50,8.2,1,28)
  CALL PLOT (9.75,8.2,1,28)
  CALL SYMBOL (4.3,8.55,0.,.12,20,CUTOUT)
  CALL VECTORS
  RETURN
  END

```


73/74 OPT=1 TRACE

FTN 4.6+452

```

SUBROUTINE NLLSQPT (Y,3,NPARMS,NPLT,NZERO1,NTOT,YMAX,YMIN,RES,
1TITLE,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 FLOTYPE(NTYPE)
  JCOUNT = MOD(NPLT - 1,4)
  XOFF = 2.
  YOFF = 2. + 10.*JCOUNT
  CALL SIZE(26.,YOFF+8.)
C
C  DRAW BOX AROUND THE DATA AND MODEL PLOT
C
C    CALL BOX(XOFF,YOFF)
C
C  AUTOSCALE Y IF YMAX EQUALS ZERO
C
  IF (YMAX.NE.0.) GO TO 2
  YMIN = YMAX = Y(NZERO1)
  DO 1 I=NZERO1,NTOT
    IF (Y(I).LT.YMIN) YMIN = Y(I)
1    IF (Y(I).GT.YMAX) YMAX = Y(I)
2    CONTINUE
300  XMAX=NTOT
    XMIN=NZERO1
    XDIF=XMAX-XMIN
    YDIF=YMAX-YMIN
    YMIN=YMIN-(.50*YDIF)
    YMAX=YMAX+(.50*YDIF)
    YDIF=YDIF*2.0
    XSCAL=8.5455/XDIF
    YSCAL=6.5636/YDIF
    CALL VECTORS
    CALL SCALE (XSCAL,YSCAL,XOFF,YOFF,XMIN,YMIN)
    XXDIS=.24/XSCAL
    XYDIS=.80/XSCAL
    YXDIS=.24/YSCAL
    YYDIS=.80/YSCAL
C
C    DRAW X AXIS FOR DATA PLOT
C
  ENCODE (4,310,ARRAY) XMIN
310  FORMAT(F4.0)
    CALL SYMBOL (XMIN-XXDIS,YMIN-YXDIS,0.,.16,4,ARRAY)
    CALL PLOT (XMIN,YMIN,0,0)
    CALL PLOT (XMIN,YMIN,1,8)
    XP=IXP=NZERO1/10
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 (4,310,ARRAY) XMAX
    CALL SYMBOL (XMAX-XXDIS,YMIN-YXDIS,0.,.16,4,ARRAY)
    CALL PLOT (XMIN,YMIN,0,0)

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

C
C      DRAW AND LABEL Y AXIS FOR DATA PLOT
C
      YP=IYP=YMIN
      IPP=YMIN+.5
      YLMK=YIP+1.
      YHMK=IHP=YMAX
      YP=YP+.5
      IF (IYP.NE.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.LT.YHMK) GO TO 340
      IF (YP.GE.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-YYDIS,0.,.16,4,ARRAY)
      ENCODE (4,310,ARRAY) YHMK
      CALL SYMBOL (XMIN-XYDIS,YHMK-YYDIS,0.,.16,4,ARRAY)
      ENCODE (72,20,ARRAY) (TITLE(I),I=1,9)
      CALL SYMBOL (XMIN,YMAX,0.,.12,72,ARRAY)
C
C      PLOT DATA
C
      CALL POINTS
      DO 370 I=NZERO1,NTOT
      FI=I
370    CALL PLOT (FI,Y(I),1,1)
C
C      PLOT MODEL AS Y(I) - RES(I)
C
      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)
C
C      DRAW VERTICAL LINE TO INDICATE POSITION AND HEIGHT OF EACH PEAK
C
      DO 460 I=2,NPARMS,3
      CALL PLOT (B(I+2),B(1),0,0)
      CALL PLOT (B(I+2),B(1),1,5)
      CALL PLOT (B(I+2),B(1)-B(I),1,5)
      HT2 = B(1)-B(I)/2.
      GAM2 = B(I+1)/2.
      CALL PLOT(B(I+2)-GAM2,HT2,0,0)
      CALL PLOT(B(I+2)-GAM2,HT2,1,7)
460    CALL PLOT(B(I+2)+GAM2,HT2,1,7)
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

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

700  FORMAT (4X, #CAL CONST = #, F10.7, # MM/SEC/CH#, 5X, #CG = #, F10.4,
      I# CHANNELS#)
      CALL SYMBOL (XMIN, YMAX - (.2/YSCAL), 0...12, 65, ARRAY)
C
C  THIS CODE GENERATES THE VELOCITY AXIS ON THE DATA PLOT
C  IF CG IS NON-ZERO.  FOR THIS SECTION, THE FOLLOWING
C  PARAMETERS ARE IMPORTANT.
C
C      VELMIN=MINIMUM IN VELOCITY CORRESPONDING TO XMIN.
C      VELMAX=MAXIMUM IN VELOCITY CORRESPONDING TO XMAX.
C      VAX=OFFSET OF VELOCITY AXIS ABOVE CHANNEL AXIS.
C          (.5 INCHES ABOVE)
C      VLMK=LOW VALUE ON VEL AXIS TO BE LABELED.
C      VHMK=HIGH VALUE ON VEL AXIS TO BE LABELED.
C
C  SET UP INITIAL PARAMETERS REQUIRED.
C
      VELMIN = (XMIN-CG)*VELC
      VELMAX = (XMAX-CG)*VELC
      VEL1 = 1./VELC
      VLMK = IVL = VELMIN
      DEL = VLMK - VELMIN
      VAX = .5/YSCAL + YMIN
      VHMK = IVH = VELMAX
C
C  DRAW VELOCITY AXIS.
C
      CALL PLOT(XMIN, VAX, 0, 0)
      VPOS = XMIN + DEL/VELC
800   CALL PLOT(VPOS, VAX, 1, 8)
      VPOS = VPOS + VEL1
      IF (VPOS.LE.XMAX) GO TO 800
      CALL PLOT(XMAX, VAX, 1, 0)
C  LABEL VELOCITY AXIS AT VLMK, 0. AND VHMK
      VPOS = CG - .04/XSCAL
      CALL SYMBOL(VPOS, VAX-YXDIS, 0...16, 1, 1H0)
      VPOS = CG + VLMK * VEL1
      ENCODE (3, 820, ARRAY) IVL
820   FORMAT (I3)
      CALL SYMBOL (VPOS-.32/XSCAL, VAX-YXDIS, 0...16, 3, ARRAY)
      VPOS = CG + VHMK * VEL1
      ENCODE (3, 820, ARRAY) IVH
      CALL SYMBOL (VPOS-.32/XSCAL, VAX-YXDIS, 0...16, 3, ARRAY)
C
C  DRAW VERTICAL LINE AT VEL =0.
C
      CALL PLOT (CG, 100., 0, 0)
      CALL PLOT (CG, VAX, 1, 0)
600   CONTINUE
C  PRINT OUT LORENTZ INFO ON PLOT
C
      ENCODE (18, 100, ARRAY) B(1)
100   FORMAT (2X, #8KG = #, F10.5)
      CALL SYMBOL(XMIN, YMAX-.4/YSCAL, 0...12, 18, ARRAY)
      K=1
      L = 2
      DO 120 I=2, NPARMS, 3

```

73/74 OPT=1 TRACE

FTN 4.6+452

```

C
C  CHANGE GAMMA AND POS TO VELOCITY UNITS IF CALIBRATION INFO AVAILABLE
C
      IF (VELC.EQ.0.) GO TO 1001
      B(I+1) = B(I+1) *VELC
      B(I+2) = (B(I+2)-CG)* VELC
1001  ENCODE (70,110,ARRAY) K,B(I),K,B(I+1),K,B(I+2)
110   FORMAT (2X,HT,I1,*,*,G14.7,2X,GAMMA,I1,*,*,G14.7,
12X,POS,I1,*,*,G14.7)
      K=K+1
      L = L + 1
      IF (L.EQ.8) L = 25
      CALL SYMBOL (XMIN,YMAX-(L*.2/YSCAL),0.,.12,70,ARRAY)
120   CONTINUE
      XOFF = 15.
C
C  DRAW BOX AROUND THE RESIDUAL PLOT
C
      CALL BCX(XOFF,YOFF)
C
C  START RESIDUAL PLOT WORK BY AUTOSCALING RES
C
      RESMIN = RESMAX = 0.
      DO 500 I=NZERO1,NTOT
      IF (RES(I).GT.RESMAX) RESMAX = RES(I)
500   IF (RES(I).LT.RESMIN) RESMIN = RES(I)
      RDIF = RESMAX - RESMIN
      IF (RDIF.LT.0.1) RDIF = 0.1
      RSCAL = 6.5636/(RDIF*2.)
      CALL SCALE (XSCAL,RSCAL,XOFF,YOFF,XMIN,-RDIF)
      RXDIS=.24/RSCAL
      RROIS=.08/RSCAL
C
C  DRAW AND LABEL X AXIS FOR RESIDUAL PLOT
C
      ENCODE (4,610,ARRAY) XMIN
      FORMAT(F4.0)
610   CALL SYMBOL (XMIN-RXDIS,-RXDIS,0.,.16,4,ARRAY)
      CALL PLOT (XMIN,0.,0,0)
      CALL PLOT (XMIN,0.,1,8)
      XP=IXF=NZERO1/10
620   XP=XP+10.
      IF (XP.GE.XMAX) GO TO 630
      CALL PLOT (XP,0.,1,8)
      GO TO 620
630   CALL PLOT (XMAX,0.,1,8)
      ENCODE (4,610,ARRAY) XMAX
      CALL SYMBOL (XMAX-RXDIS,-RXDIS,0.,.16,4,ARRAY)
C
C  DRAW Y AXIS FOR RESIDUAL PLOT
C
      CALL PLOT (XMIN,0.,0,0)
      R=0.
510   CALL PLOT (XMIN,R,1,6)
      R=R+.1
      IF (R.LT.RDIF) GO TO 510
      CALL PLOT (XMIN,RDIF,1,0)

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73/74 OPT=1 TRACE

FTN 4.6+452

```

      CALL PLOT (XMIN,3.,0.0)
      R= -.1
530   CALL PLOT (XMIN,R,1,6)
      R = R -.1
      IF (R.GT.-RDIF) GO TO 530
      CALL PLOT (XMIN,-RDIF,1,0)
C
C   LABEL Y AXIS
C
      RLABEL = R + .1
      R=RLABEL
525   ENCODE (4,520,ARRAY) RLABEL
520   FORMAT (F4.1)
      CALL SYMBOL (XMIN-XYDIS,RLABEL-RRDIS,0...16,4,ARRAY)
      RLABEL=RLABEL-R
      IF (RLABEL.LE.RDIF)GO TO 525
C
C   WRITE TITLE ON RES PLOT
C
      ENCODE (72,20,ARRAY) (TITLE(I),I=1,9)
      CALL SYMBOL (XMIN,RDIF,0...12,72,ARRAY)
      NPEAKS = NPARMS/3
      ENCODE(19,900,ARRAY) NPEAKS
900   FORMAT (# FOR #,I2,# PEAK MODEL#)
      CALL SYMBOL (XMIN,RDIF-.2/RSCAL,3...12,19,ARRAY)
20    FORMAT (10A8)
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

```