An electron paramagnetic resonance study of iron(+3) in single crystals of topaz.

Stuart Milton Quick
University of Windsor

1-1-1966

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation
https://scholar.uwindsor.ca/etd/6445

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000 ext. 3208.
AN ELECTRON PARAMAGNETIC RESONANCE STUDY OF Fe$^{3+}$
IN SINGLE CRYSTALS OF TOPAZ

A Thesis
Presented to
the Faculty of the Department of Physics
University of Windsor

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Stuart Milton Quick
September 1966
The electron paramagnetic resonance (EPR) spectrum of Fe$^{3+}$ in topaz has been investigated at x-band frequencies at room temperature (290 °K.) and liquid helium temperature (4.2 °K.). It has been interpreted on the assumption that Fe$^{3+}$ occupies the eight equivalent Al$^{3+}$ sites in topaz. The spectrum shows large superhyperfine structure (SHFS) in addition to large zero-field splitting. The constants of the orthorhombic spin Hamiltonian which fit the spectrum to a good approximation are $g_x = 2.0028$, $g_y = 2.0015$, $g_z = 2.0011$, $b_2^0 = 3.445$ kg., $b_2^2 = 2.594$ kg., $b_4^0 = 0.061$ kg., $b_4^2 = 0.147$ kg., $b_4^4 = 0.008$ kg. The separation between the outer components of the SHFS is as much as 300 gauss for some orientations of magnetic field.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. THEORY</td>
<td>1</td>
</tr>
<tr>
<td>Introduction</td>
<td>2</td>
</tr>
<tr>
<td>The Fine Structure</td>
<td>4</td>
</tr>
<tr>
<td>(a) Weak crystal fields</td>
<td>6</td>
</tr>
<tr>
<td>(b) Strong crystal fields</td>
<td>10</td>
</tr>
<tr>
<td>The SHFS</td>
<td>14</td>
</tr>
<tr>
<td>Experimental Results Inferred From the Theory</td>
<td>15</td>
</tr>
<tr>
<td>II. INSTRUMENTATION</td>
<td>18</td>
</tr>
<tr>
<td>III. CRYSTALLOGRAPHY AND CRYSTAL ALIGNMENT</td>
<td>23</td>
</tr>
<tr>
<td>Crystallography</td>
<td>23</td>
</tr>
<tr>
<td>General data</td>
<td>23</td>
</tr>
<tr>
<td>The X-ray analyses</td>
<td>24</td>
</tr>
<tr>
<td>Structure and space group</td>
<td>24</td>
</tr>
<tr>
<td>EPR results inferred from the structure</td>
<td>27</td>
</tr>
<tr>
<td>Crystal Alignment</td>
<td>27</td>
</tr>
<tr>
<td>Alignment using X-rays</td>
<td>27</td>
</tr>
<tr>
<td>Alignment in the magnetic field</td>
<td>29</td>
</tr>
<tr>
<td>IV. EXPERIMENTAL PROCEDURE</td>
<td>34</td>
</tr>
<tr>
<td>Mounting the Crystal on the Cavity Pin</td>
<td>34</td>
</tr>
<tr>
<td>Locating the Crystallographic Axes</td>
<td>35</td>
</tr>
<tr>
<td>Locating the Spectral Axes</td>
<td>36</td>
</tr>
<tr>
<td>Plotting the Angular Variations</td>
<td>38</td>
</tr>
<tr>
<td>Identifying the Spectral Axes</td>
<td>39</td>
</tr>
</tbody>
</table>

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
CHAPTER

Measuring Resonant Fields ............................................ 40
Analysing the Fine Structure Spectra ............................ 42
Studying the SHFS ..................................................... 44
V. EXPERIMENTAL RESULTS AND INTERPRETATION ....... 45
The Fine Structure ...................................................... 45
The SHFS ................................................................. 62
VI. DISCUSSION AND CONCLUSIONS ........................... 69
Discussion ................................................................. 69
Conclusions ............................................................... 72
ACKNOWLEDGMENTS .................................................. 74
REFERENCES ............................................................. 75
VITA AUCTORIS ......................................................... 76
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Matrix of the Spin Hamiltonian in ( S = 5/2 ) Manifold</td>
<td>7</td>
</tr>
<tr>
<td>II. Resonance Fields in Kgauss and Effective G Values of Fe(^+3) EPR Fine Structure Lines in Topaz at X-Band Frequencies</td>
<td>49</td>
</tr>
<tr>
<td>III. Direction Cosines of the Set of Spectral Axes</td>
<td>54</td>
</tr>
<tr>
<td>IV. Constants of the Spin Hamiltonian</td>
<td>57</td>
</tr>
<tr>
<td>V. Errors of Fit of Measured Resonant Fields With Energy Levels</td>
<td>57</td>
</tr>
<tr>
<td>VI. Changes in Relative Intensities With Decreasing Temperature</td>
<td>63</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Orientation of $\vec{h}$ and $\vec{H}$</td>
<td>9</td>
</tr>
<tr>
<td>2. Straight-Detection X-Band EPR Spectrometer</td>
<td>19</td>
</tr>
<tr>
<td>3. The TE$_{102}$ Reflection Cavity and Rotating Mechanism</td>
<td>20</td>
</tr>
<tr>
<td>4. Crystal Structure of Topaz Projected onto (100) Plane</td>
<td>25</td>
</tr>
<tr>
<td>5. Illustration of the Use of the Wulff Net</td>
<td>31</td>
</tr>
<tr>
<td>6. Stereographic Projection Showing the Crystallographic Axes and the Fe$^{+3}$ Spectral Axes in Topaz</td>
<td>46</td>
</tr>
<tr>
<td>7. Rotation Pattern of the EPR Spectra at X-Band Frequency with $\vec{H}$ Rotated in the Quarter Spectral Planes in Topaz</td>
<td>47</td>
</tr>
<tr>
<td>8. The X and Y Components of the Effective $g^i$ Tensor As Functions of $\eta$</td>
<td>50</td>
</tr>
<tr>
<td>9. The EPR Spectrum in Topaz at X-Band Frequency and 290 Degrees $\mathbf{K}$</td>
<td>52</td>
</tr>
<tr>
<td>10. Stereographic Projection of the Fe$^{+3}$ Site I</td>
<td>56</td>
</tr>
<tr>
<td>11. The EPR Spectrum in Topaz at X-Band Frequency and 4.2 Degrees $\mathbf{K}$</td>
<td>58</td>
</tr>
<tr>
<td>12a. Energy Level Diagram for the Magnetic Field Along the X Axis</td>
<td>59</td>
</tr>
</tbody>
</table>
FIGURE PAGE

12b. Energy Level Diagram for the Magnetic Field Along the Y Axis ..................................................... 60

12c. Energy Level Diagram for the Magnetic Field Along the Z Axis ....................................................... 61

13. Typical XY Plotter Recordings of the SHFS in Topaz ................................................................. 64

14. Angular Variations of the SHFS Splitting ........ 65

15. SHFS Splitting of the Fine Structure Line a for Three Orientations of Magnetic Field in the Region of the X Axis ...................................................... 67
CHAPTER I

THEORY

The quantity of theoretical literature which has been published in the field of electron paramagnetic resonance (EPR) is very extensive. Therefore, only that theory is presented here, which is essential for the analysis of the EPR fine structure spectrum which results when an Fe$^{3+}$ ion substitutionally replaces the Al$^{4+}$ ion in the topaz crystal. The results of the experiment confirm the interpretation that the Fe$^{3+}$ ion substitutes, as an impurity for the Al$^{4+}$ ion of topaz in the natural state. For the purpose of a brief introduction to the field of EPR, the concepts leading to the use of a spin Hamiltonian are discussed qualitatively. The theory necessary for the interpretation of the observed fine structure is presented in detail. The mechanism of the superhyperfine structure (SHFS), which is expected to be observed in addition to the fine structure, is discussed qualitatively. Then, experimental results which can be inferred from the theory are discussed, together with certain conventions which were used in the analysis. The theory for the analysis of the fine structure follows that presented in the papers by Manoogian et al. (1965) and by Holuj (1966) unless otherwise indicated. The detailed theory for the analysis of the SHFS is not presented.
I. INTRODUCTION

The experimentally-observed EPR spectrum resulting from an ionic impurity in a crystalline solid is commonly described by a Hamiltonian operator, called a spin Hamiltonian. The coefficients of the operator terms which make up the spin Hamiltonian are functions of the interactions of the paramagnetic ion with the crystalline field, spin-orbit coupling, spin-spin coupling, and other interactions on the ion. The ability to measure directly these coefficients, in the experiment, eliminates the necessity of determining the contribution of each separate interaction. The energy levels which the ion may possess due to the many interactions are given by the eigenvalues of this operator.

The derivation of the spin Hamiltonian is as follows. Abragam and Pryce (1951) incorporated all the interactions that an ion experiences in a crystalline environment into a unified theory concerned with explaining the appearance of nuclear hyperfine structure in EPR. The total Hamiltonian is the sum of all these interactions and is given by

\[ W = W_F + V + W_{LS} + W_{SS} + \beta H_s (L + 2S) + W_N - \gamma \beta H_s I \]

The terms have been written in the order of decreasing magnitude for the iron group of the transition elements. \( W_F \) describes the coulomb repulsion between the magnetic electrons, and the coulomb attraction between the magnetic electrons and the nucleus of the paramagnetic ion. \( V \)
is the crystal field potential and describes the electric field which is generated by the diamagnetic ion neighbors, called ligands, of the paramagnetic ion. $W_{LS}$ is the spin-orbit coupling; and $W_{SS}$ is the spin-spin coupling. The next term describes the interaction between the magnetic electrons and the applied magnetic field. $W_{N}$ describes the magnetic interaction between the magnetic electrons and the magnetic moment of the nucleus along with the electrostatic interaction between the magnetic electrons and the electric quadrupole moment of the nucleus. The last term describes the interaction between the magnetic moment of the nucleus and the applied magnetic field.

For the iron group, the magnitude of the crystal field is described as intermediate because $V$ generally lies between $W_{P}$ and $W_{LS}$ in decreasing order of magnitude. Next to $W_{P}$, the crystal field is dominant because the magnetic electrons are in 3d orbits and are not shielded. In practice, it is also possible to distinguish three different degrees of crystal field strength within the iron group; and this is done below.

In order to derive the spin Hamiltonian, from the above form, the variables of each term are replaced by the appropriate angular momentum operators (Stevens 1952). The energy levels of the system are the eigenvalues of this operator and are obtained by applying perturbation theory.
The free ionic ground state of Fe$^{3+}$ is $3d^5$ $^6S_{5/2}$.

Clearly, the ground state is only six-fold spin degenerate where $S = 5/2$ is the true electronic spin value. In a complicated mechanism which is still uncertain, a crystal field of non-cubic symmetry along with admixtures of other terms and configurations splits this spin sextet into three doublets called Kramers doublets. The main purpose of this experiment is to study the effect of the static crystal field on these Kramers doublets.

II. THE FINE STRUCTURE

The following spin Hamiltonian describes the fine structure spectra resulting from an $S$-state Fe$^{3+}$ ion in an orthorhombic crystal field.

(1) $H(S) = \beta H g \cdot S + \frac{1}{3} b_2^0 o_2^0 + \frac{1}{3} b_2^2 o_2^2 + \frac{1}{60} b_4^0 o_4^0 + \frac{1}{60} b_4^2 o_4^2 + \frac{1}{60} b_4^4 o_4^4$.

This spin Hamiltonian is expressed in a coordinate system defined by three orthogonal axes, called the spectral axes. The first term describes the interaction of the applied magnetic field with the electron spin and is called the Zeeman term. In general, the g value is a tensor having diagonal form, in this coordinate system, with the principal values $g_x$, $g_y$, $g_z$. The crystal field described by the spin
Hamiltonian of eq. (1) is considered orthorhombic in the sense that the spin operators are all of even order. Each of the spin operators, $O^m_n$, describes a different type of crystal field symmetry which contributes to the overall symmetry. In order for the spin Hamiltonian to be accurate, it must, first of all, reflect the symmetry of the paramagnetic ion it describes. Since, in most cases, the exact expression of the crystal field potential is unknown, the practical procedure is to include those spin operators which describe the local symmetry of the paramagnetic ion to the best approximation. The operators in eq. (1) were chosen in accordance with the local symmetry of the Fe$^{3+}$ ion in topaz. This symmetry is $C_1$, which is evident from Fig. (10). We assume that the replacement of the Al$^{3+}$ ion by the Fe$^{3+}$ ion causes no great distortion from the form shown in this figure. Clearly, $C_1$ admits of only the identity element so we must make certain approximations to obtain a higher symmetry. From the figure it is evident that two oxygen ions and two fluorine ions lie approximately in a plane. Also, the upper and lower aluminum-oxygen bond directions are almost normal to this plane. This means that the coefficients of the odd order spin operator terms must be small. Also, the fact that the wave functions are d-functions eliminates operator terms greater than the fourth order. Therefore, it is expected that the crystal field set
up by the ligands is orthorhombic to a good approximation. The terms in \( b_2^0 \) and \( b_4^0 \) describe the axial contribution; the terms in \( b_2^2 \) and \( b_4^2 \) describe the rhombic contribution; and the term in \( b_4^4 \) describes the cubic contribution. These operators have been listed by Orbach (1961). The matrix elements of the operators for various spin multiplets can be found in Low (1960) and Jones et al. (1959).

The effect of the crystal field on the Kramers doublets can be divided into three classes: (a) strong crystal fields, when the crystal field terms are dominant and the Zeeman term can be considered as a perturbation; (b) weak crystal fields, when the Zeeman term is dominant and the crystal field terms can be considered as a perturbation; and (c), intermediate crystal fields, when the crystal field terms and the Zeeman term are of the same order of magnitude. The analysis of this last class is very complex because perturbation theory does not apply.

A brief review of (a) and (b) is now given since the theory associated with each applies, in part, to this experiment. This is because the crystal field at the site of the Fe\(^{3+}\) impurity in topaz is of intermediate strength.

(a) Weak Crystal Fields

The matrix of the spin Hamiltonian in eq. (1), in the \( S = 5/2 \) manifold, considering the crystal field terms as the perturbation, is shown in Table I. The magnetic field is
**TABLE I**

Matrix of the spin Hamiltonian in $S = 5/2$ manifold

<table>
<thead>
<tr>
<th>$\pm \frac{5}{2}$</th>
<th>$\pm \frac{1}{2}$</th>
<th>$\pm \frac{3}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pm \frac{5}{2}$</td>
<td>$\pm \frac{10b_2^0}{3} + b_4^0$</td>
<td>$\frac{10b_2^0}{3} + \frac{10b_4^2}{20}$</td>
</tr>
<tr>
<td>$\pm \frac{1}{2}$</td>
<td>$\frac{10b_2^0}{3} + \frac{10b_4^2}{20}$</td>
<td>$\frac{5b_4^2}{5}$</td>
</tr>
<tr>
<td>$\pm \frac{3}{2}$</td>
<td>$\frac{5b_4^2}{5}$</td>
<td>$\sqrt{b_2^2 - b_4^2}$</td>
</tr>
</tbody>
</table>
taken in the Z direction. The Hamiltonian takes a simple form with the magnetic field in this direction since the Zeeman term is diagonal.

If, however, the magnetic field is oriented in any other direction, the Zeeman term will not be diagonal in the coordinate system of the crystal field axes. To achieve diagonalization, the Hamiltonian is expressed in a new coordinate system whose z axis is the quantization axis of the electron spin. Upon the application of an external magnetic field at the spherical coordinates Θ and Φ with respect to the crystal field axes, the electron spin is immediately quantized along a specific direction. If g were isotropic, the Zeeman term could be written

$$\beta g \vec{H} \cdot \vec{S} = \beta g H_0 \hat{n} \cdot \vec{S}$$

and the electron spin would then be quantized along a direction defined by the unit vector $\hat{n}$ in the direction of the magnetic field. However, in general, g is a diagonal tensor. Therefore, the Zeeman term must be written

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

where g has the diagonal diadic form $g = g_{xx} \hat{i} \hat{i} + g_{yy} \hat{j} \hat{j} + g_{zz} \hat{k} \hat{k}$. Thereupon the electron spin is quantized along a direction defined by the vector.

$$\beta H_0 \hat{g} \cdot \hat{n} = \beta (g_{xx} \hat{H}_x \hat{i} + g_{yy} \hat{H}_y \hat{j} + g_{zz} \hat{H}_z \hat{k}) = \vec{h}$$

This h vector may be defined by the angles β and α with respect to the crystal field axes as shown in Fig. 1.
Fig. 1. Orientation of $\mathbf{H}$ and $\mathbf{H}$. Orientation of the electron spin quantization axis $\mathbf{H}$, when the spectroscopic splitting factor $g$ is a tensor, for a magnetic field $\mathbf{H}$ applied at the Euler angles $\Theta$ and $\Phi$ with respect to the crystal field axes.
Therefore, the Zeeman energy proves to be diagonal in a coordinate system rotated relative to the original by angles \( \beta \) and \( \alpha \). In the new coordinate system, the Hamiltonian in eq. (1) take the form

\[
H(S) = \beta H_0 g_\alpha S_z + \frac{1}{3} \sum_{m=0}^{2} A_{2m}^2 O_{2m}^m + \frac{1}{60} \sum_{m=0}^{2} A_{4m}^2 O_{4m}^m \quad \alpha = x, y, z
\]

where the new coefficients are functions of the old coefficients, \( b_n^m \), and the appropriate angular functions. These have been listed by Vinokurov et al. (1964).

The energy levels which can be calculated by diagonalizing the matrix in Table I using perturbation theory are not given since the entire process of diagonalization and calculation of energy levels was performed by an IBM 1620 electronic computer. This procedure is described in Chapter IV.

(b) Strong Crystal Fields

In this case, the Zeeman term is assumed to be smaller than the remaining terms of the Hamiltonian. Clearly, the effect of the crystal field on the Kramers doublets is obtained by studying the zero-field spin Hamiltonian. The zero-field spin Hamiltonian of eq. (1) yields two identical 3 by 3 matrices in the \( S = 5/2 \) manifold. These are, of course, of the form given in Table I with \( H_z = 0 \). The process of diagonalizing these matrices, whose elements are regarded as functions of the parameters

\[
\eta = \frac{b_2^2}{\sqrt{3} b_0^2}
\]
and \( b_2^0 \), involves solutions of two identical cubic equations. The solution of these can only be attempted using numerical analysis. The three doubly-degenerate levels obtained upon a numerical solution of these equations are of the form

\[
E_i^0 = \omega_i b_2^0
\]

where \( \omega_i \) is a function of \( \eta \) and \( i \) refers to one of the three doublets. These three doublets are the Kramers doublets. The eigenfunctions corresponding to each doublet have the form

\[
| \pm \frac{1}{2} \rangle = a_1^1 | \pm \frac{1}{2} \rangle + a_2^2 | \mp \frac{3}{2} \rangle + a_3^3 | \pm \frac{5}{2} \rangle
\]

Each doublet is assumed isolated and belonging to the effective spin \( S' = 1/2 \) and each possessing the highly anisotropic g factor, \( g^1 \). The effect of the magnetic field of each \( i \)th doublet can be described by the following spin Hamiltonian

\[
H(S) = g^1 H_x S_x' + g^1 H_y S_y' + g^1 H_z S_z'
\]

where \( S' = 1/2 \) to a first order of approximation.

We have discussed earlier the procedure of expressing the Hamiltonian of eq. (1) in the form of eq. (2) in order that the Zeeman energy is diagonalized. This was done by transforming the spin operators, in terms of the Euler angles, into a coordinate system whose z axis is the quantization axis of the electron spin. This is equivalent to a rotation of the coordinate system. The eigenfunctions in
the new system have the general form of eq. (4). An equi-
valent method of diagonalizing the Hamiltonian is to trans-
form the eigenfunctions of eq. (4) back into the old system
in which the Hamiltonian of eq. (1) is defined and to ex-
press this transformation by means of the same Euler angles.
This is equivalent to a rotation of the quantization axis.
We find this latter procedure more convenient in the dis-
cussion of strong crystal fields. Since each pair of
functions can be rotated independently, assuming \( S^f = 1/2 \),
they can be transformed like the two partners of a two di-
mensional representation of the rotation group (Tinkham 1964).
Assuming the rotation is through the Euler angles \((\alpha, \beta, 0)\)
defined according to Tinkham (1964), the wave functions are
\[
\begin{align*}
|11\rangle &= \exp \left[ \frac{i\alpha}{2} \cos \theta \right] |+ 1\rangle + \exp \left[ \frac{i\alpha}{2} \sin \beta \right] |- 1\rangle \\
|21\rangle &= -\exp \left[ \frac{i\alpha}{2} \sin \beta \right] |+ 1\rangle + \exp \left[ \frac{-i\alpha}{2} \cos \beta \right] |- 1\rangle 
\end{align*}
\]
where, \(|\pm 1\rangle\) are the two components of the doublet when the
quantization axis is parallel to the \(Z\) spectral axis
\((\alpha = \beta = \gamma = 0)\).

We can now calculate the matrix elements of the Zeeman
term \(\hbar \vec{S} \cdot \vec{H} \) in the manifold of the \(|ki\rangle\), which are the
zeroth-order wave functions. The \(k\) refers to one of the two
components of the \(i^{th}\) doublet. We obtain:
\[
\begin{align*}
\langle kj | \hbar \vec{S} | ki \rangle &= (-1)^{k+1} \left\{ \langle + j | \hbar \vec{S} | + 1 \rangle \cos \beta + \frac{1}{2} \sin \beta \right. \\
&\left. \left( e^{-i\gamma} \langle + j | \hbar \vec{S} | - 1 \rangle + e^{i\gamma} \langle - j | \hbar \vec{S} | - 1 \rangle \right) \right\}
\end{align*}
\]
where

\[ \langle \pm j|\vec{H}\cdot\vec{S}|\pm i\rangle = \frac{1}{2} h_2^{ij} \quad \text{for } i \neq j \]

\[ = \frac{1}{2} h_2^i \quad \text{for } i = j \]

and

\[ \langle \pm j|\vec{h}\cdot\vec{S}|\pm i\rangle = \pm \frac{1}{2} h_z^{ij} \quad \text{for } i \neq j \]

\[ = \pm \frac{1}{2} h_z^i \quad \text{for } i = j \]

Here, \( h_2^{ij} = \beta g_x^i H_x G_x^{ij} \) and \( h_z^{ij} = \beta g_z^i H_z G_z^{ij} \)

and

\[ G_z^{ij} = (a^1_j a^1_i - 3 a^2_i a^2_j + 5 a^3_i a^3_j) = G_i^j \]

\[ G_x^{ij} = \pm 3 a^1_j a^1_i + 2 \sqrt{2} (a^1_j a^1_i + a^2_j a^1_i) \]

\[ \pm \sqrt{5} (a^3_j a^2_i + a^3_i a^2_j) = G_x^{ij} \]

Eq. (10) clearly holds only in the case when the Zeeman term is much smaller than the crystal field terms. When the Zeeman term approaches the magnitude of the crystal field terms, which may occur when the magnetic field is increased in the course of the experiment, we may no longer assume each Kramers doublet isolated. Each wavefunction in eq. (6)
must include contributions from the wavefunctions associated with the other doublets.

III. THE SHFS

The symmetry of the octahedral environment of the Fe$^{3+}$ impurity in topaz is $C_1$. This means that the two F$^{19}$ nuclei appear inequivalent to the Fe$^{3+}$ ion. Therefore, the magnetic electrons of the Fe$^{3+}$ ion will interact with each F$^{19}$ nucleus independently. From preliminary calculations, it appears that the observed SHFS may be explained by adding to the Hamiltonian of eq. (1) a Hamiltonian for each $a$ th F$^{19}$ nucleus:

\begin{equation}
H_a = (S.A_a + \gamma \frac{S}{\mu_H} \cdot I_a) \ a = 1, 2.
\end{equation}

The calculations are complicated in that the effective magnetic field seen by each nucleus is the quantity in brackets. This effective field is a tensor and lies in yet a different direction than that of $\mathbf{H}$ or $\mathbf{\hat{H}}$. The F$^{19}$ nucleus has the nuclear spin $I = 1/2$. Therefore, in a very general qualitative manner, we would expect each fine structure line to be split into four lines, one the resultant of two states with $m_I = 1/2$ (spin up), another the resultant of two states with $m_I = -1/2$ (spin down) and two the resultants of combinations of both states. Since the two F$^{19}$ nuclei are inequivalent, it follows that these last two combinations should be different. In general, therefore, we expect that the
superhyperfine interaction should manifest itself in quartet splitting of the fine structure lines.

IV. EXPERIMENTAL RESULTS INFERRED FROM THE THEORY

The spin Hamiltonian matrix in Table I can be converted to fit the other spectral axes by substituting for the coefficients $b^m_n$, the coefficients listed by Vinokurov et al. (1964). To first order, by substituting the transformed diagonal coefficients, it is apparent that the resonances are most widely separated when the magnetic field is parallel to the Z axis, next widely separated when the magnetic field is parallel to the Y axis, and least separated when the magnetic field is parallel to the X axis, if $b_0^2$ and $b_2^2$ are taken to have the same sign and $b_0^2$ is greater than $b_2^2$. This fact will later aid in identifying the spectral axes as discussed in Chapter IV.

The transformations of the even order spin operators given in eq. (1) are symmetrical about the spectral axes for rotations in spectral planes. This means, that if, indeed, the spin Hamiltonian of eq. (1) is accurate, the variation of the resonance spectra with magnetic field will be symmetrical about the spectral axes for rotation of magnetic field in spectral planes.

In order to describe certain conventions used in this experiment we consider a simple example. From Table I the
quantum energy for the transition $5/2 \rightarrow 3/2$ is, to first order,
\[ h\nu = g_{z}^{\frac{3}{2}}H_{z} + 4b_{2}^{0} + 4b_{4}^{0} = g\beta H_{o}. \]
Here, $H_{z}$ is the value of magnetic field at which the $5/2 \rightarrow 3/2$ transition occurs for the quantum energy $h\nu$. The $g_{z}$ is the $z$ component of the effective $g$ tensor for the $5/2 \rightarrow 3/2$ transition. $H_{o}$ is the magnetic field for a free electron spin transition at this quantum energy; and $g$ is the isotropic free electron spin value. To a good approximation, the free radical diphenyl picryl hydrazyl (DPPH) occurs with the free spin value (actually 2.0036); and the resonance of this substance is commonly used as a marker. The above equation is rewritten
\[ H_{z} = \frac{g}{g_{z}}H_{o} - 4b_{2}^{0} - 4b_{4}^{0} \Rightarrow H_{o} = 4b_{2}^{0} - 4b_{4}^{0}. \]

The coefficients are now expressed in units of electron gauss. We can also put
\[ h\nu = g\beta H_{o} = g_{\text{eff}}\beta H_{z} \]
where $g_{\text{eff}}$ is the experimental effective $g$ value of the $5/2 \rightarrow 3/2$ transition.

Then
\[ g_{\text{eff}} = g\frac{H_{o}}{H_{z}} \equiv 2\frac{H_{o}}{H_{z}}. \]

This simple relation is used to determine the effective $g$ values of transitions when the resonance magnetic field of DPPH is known.
It is well known that according to the fundamental Boltzmann law of statistical mechanics, the populations $P_m$ of the energy levels are proportional to $\exp(-E_m/kT)$ where $E_m$ are the energies of the various energy levels. Thus, the lower energy levels will have the greater populations. This also means that the ratio of the intensity of a given transition between lower-lying energy levels to the intensity of a given transition between higher-lying energy levels should increase with decreasing temperature. This fact will be used to determine the absolute sign on $b_2^0$. 
CHAPTER II

INSTRUMENTATION

The EPR spectrometer used to observe the microwave absorption in topaz was of the straight-detection type (Feher 1957) employing a ferrite circulator (Gordon 1961). A block diagram of the complete spectrometer is given in Fig. 2. The spectrometer was operated at about 9.2 Ghz. (x-band) using a rectangular $\text{TE}_{102}$ reflection cavity. The magnetic field modulation frequency was 100 Khz. which was generated by an oscillator within the Princeton Research JB-5 phase-sensitive detector and lock-in amplifier. This signal was amplified and applied to a small coil about the crystalline sample inside the cavity.

For anisotropy studies, the crystal under investigation in the cavity was mounted on a pin, which by means of screw gears and drive shaft was rotated about a horizontal axis by turning a graduated tuning knob on top of the cavity-wave-guide system (Thyer 1966). This cavity and rotating mechanism is shown in detail in Fig. 3.

The klystron microwave frequency was stabilized to the cavity resonant frequency using the technique of automatic frequency control (AFC). The klystron frequency controller consisted of a 450 Khz. signal generator and a phase-sensitive detector (PSD). The 450 Khz. signal which was generated was used to frequency modulate the klystron
Fig. 2. Straight-detection x-band EPR spectrometer.
Fig. 3. The $TE_{102}$ reflection cavity and rotating mechanism.
microwave output. Then, the 450 KHz signal reflected from the cavity was detected by the AFC crystal detector, amplified, and applied to the PSD of this controller. Here, it was compared with the original modulation signal. The result was a dc error voltage proportional to the intensity and phase difference of the two signals. The dc error voltage was applied to the klystron reflector to pull the microwave frequency to coincide with the cavity resonant frequency.

The externally applied magnetic field was provided by a 7 inch Newport electromagnet mounted on a rotatable calibrated base. The water-cooled coils were energized by a current regulated power supply. Using tapered pole tips, fields of up to 10 kilogauss were obtained.

The magnetic resonance signal from the cavity was detected by the resonance crystal detector and applied to the Princeton Research PSD. By comparing this signal with the original 100 KHz modulation signal, an output was obtained proportional to the derivative of the microwave absorption. This magnetic resonance output was then displayed as the derivative of the absorption vs. magnetic field on chart recorders. For accurate anisotropy studies, an xy plotter was used whose x input was driven by a dc voltage derived from the Hall effect. The Hall probe was taped to the magnet pole face. The small dc voltage derived from the probe was then amplified by the RFL 1890 gaussmeter.
For accurate measurements of resonant fields, proton magnetic resonance was used. The frequency of the proton resonance was measured using a Hewlett-Packard electronic frequency counter.

The cavity-waveguide system was rigidly mounted on a table which, in turn, was bolted to a concrete floor. The magnet was mounted on a moveable carriage to facilitate magnetic field measurements.
CHAPTER III

CRYSTALLOGRAPHY AND CRYSTAL ALIGNMENT

I. CRYSTALLOGRAPHY

General Data

Topaz is a fluoriferous silicate of aluminum with chemical composition \( [\text{Al(F,OH)}]_2 \text{SiO}_4 \), the fluorine being replaced by hydroxyl in amounts which vary from crystal to crystal. It exhibits perfect cleavage in the (001) plane. It has a primitive orthorhombic unit cell with dimensions \( a = 4.64 \text{ Å}, b = 8.78 \text{ Å}, \) and \( c = 8.37 \text{ Å} \) with a probable error of the order 0.05 Å. It belongs to the holohedral class of rhombic crystals, possessing the space group \( \text{D}_{2h}^{16} \) or \( \text{P} \text{2}_1/\text{b} \text{2}_1/\text{n} \text{2}_1/\text{m} \) (Pbnm). The unit cell contains 4 chemical formula units; therefore, according to the symmetry elements of the space group, there exist 8 aluminum sites which are all equivalent and 4 silicon sites which are all equivalent.

The crystal structure indicates that should an impurity substitute for aluminum, the EPR should detect 4 sets of differently - oriented but equivalent spectral axes; if an impurity should substitute for silicon, the EPR should detect 2 such sets.

The EPR work was performed with natural crystals from Mexico which are of a weak yellow colour. A fairly large crystalline sample was used, of the order of 6 mm diameter.
All other operating conditions being kept approximately constant, successively larger crystal samples were investigated until this one was found giving approximately the best signal-to-noise ratio.

The X-ray Analyses

Leonhardt (1924) made the first X-ray analysis of topaz and reported the cell dimensions, the number of molecules per unit cell, and the space group. Later, Pauling (1928) proposed an ideal type of structure for topaz. In this structure, aluminum ions are situated within octahedra of four oxygen ions and two adjacent fluorine ions; and silicon ions are situated within tetrahedra of oxygen ions. Pauling's work was soon followed by the quantitative determination of the structure by Alston and West (1928a and 1928b). They confirmed the results of Leonhardt and showed that the topaz structure is a combination of hexagonal and cubic close packing, a distorted variation of the Pauling structure. No refinement of the structure data has been made since 1928.

Structure And Space Group

The structure of topaz projected onto the (100) plane is shown in Fig. 4. The edges of the unit cell are outlined by the light solid lines. Only a partial representation of the space group (Buerger 1963) is given, enough to
Fig. 4. Crystal structure of topaz projected onto the (100) plane.

\[ c = 8.37 \text{ Å} \]

\[ b = 8.78 \text{ Å} \]
illustrate the equivalence of each aluminum site and each silicon site.

The international symbol for the topaz space group, $P 2_1/b 2_1/n 2_1/m$ (Pbnm), indicates all the symmetry elements in the structure. These are two-fold screw axes parallel to the a crystallographic axis and axial glide planes normal to it, two-fold screw axes parallel to the b crystallographic axis, and diagonal glide planes normal to it, and finally, two-fold screw axes parallel to the c crystallographic axis and mirror planes normal to it.

Three of these symmetry elements are included in Fig.4: the centers of symmetry, the screw axes along the c axis, and the mirror planes. The atomic coordinates normal to the plane of the paper are shown taken with reference to a plane through the center of symmetry in the center of the cell and are expressed in Angstroms $\times 10^{-2}$. The dotted circles indicate underlying atoms. Certain oxygen atoms at the positions 194, 194, 271, and 336, have been omitted for simplicity since they overlap other atoms. The heavy dotted lines indicate ligand bond directions which aid in illustrating the eight octahedra. Those octahedra not connected by the centers of symmetry or mirror planes are equivalent due to the screw axis operation along a direction parallel to the a axis. The equivalence of the tetrahedral silicon sites is also shown in this manner.
EPR Results Inferred From The Structure

The possible spectral axes arising from impurity substitutions in those pairs of sites in Fig. 4 which are equivalent due to the inversion center in the center of the cell will be coincident. This is because those bond directions of the environments of these sites which are also related by the inversion symmetry are parallel. There are four such differently-oriented pairs of octahedral sites and two such differently-oriented pairs of tetrahedral sites. Consequently, in the event that an impurity has substituted for the aluminum ion, the EPR should detect four sets of spectral axes which are oriented in different directions but which are equivalent. In the event that an impurity has substituted for the silicon ion, the EPR should detect two such sets.

II. CRYSTAL ALIGNMENT

Alignment Using X-rays

Before inserting the crystal into the cavity, the crystallographic axes were located. These axes are commonly taken as references in defining the directions of the spectral axes in the crystal. The c axis was located approximately by inspecting the natural cleavage in the (001) plane. The a and b axes were identified using the well-known techniques of X-ray Laue, and rotation photography (Barrett 1952).
The crystal was aligned in the X-ray beam by means of a goniometer. This device enabled crystal movement about orthogonal horizontal axes through about 45 degrees. Also, the whole goniometer was rotatable about a vertical axis. As a result of these three crystal movements, the X-ray beam could be directed through any part of the crystal. A flat plate camera was used for both types of photography. For rotation photographs, the goniometer was rotated continuously at constant speed by a small electric motor.

First, rotation photographs were taken with the crystal rotated about the approximate position of the c axis determined visually. In this manner, the c axis was oriented as closely perpendicular to the X-ray beam as possible. This condition was indicated by the sharply-defined zone lines of the rotation photograph. Since the unit cell of topaz is orthorhombic and the crystallographic axes are orthogonal, the other two axes were found by rotating the crystal about this c axis to various stationary positions and there taking backscattered Laue photographs. The positions at which the X-ray beam was directed parallel to these other axes were indicated by symmetrical Laue patterns. In turn, pins were glued parallel to these axes and the above rotational procedure was repeated. From the sharply-defined rotation photographs the following measurements were made: 4.53 ± 0.20 Å for one axis, and 8.68 ± 0.20 Å for
the other. Within the experimental error, these values compare favorably with the most accurate available if the former axis is taken as a and the latter is taken as b.

The positions of these axes were then marked on the crystal so that it could be properly oriented in the cavity. The crystal was placed in the cavity with the magnetic field oriented roughly parallel to a desired axis. Then, the final orientation with respect to crystallographic axes was made using the rotational mechanism of the cavity and plotting the positions of the axes on a Wulff net. This technique is now described.

Alignment In The Magnetic Field

As has been stated in Chapter II, the resonant cavity used in this experiment was equipped with a rotating mechanism whereby the crystal could be rotated about a horizontal axis. Then, in conjunction with this rotation, the magnetic field could be rotated about a vertical axis so that the magnetic field could be directed through the crystal in any direction. By means of a Wulff net, this direction was defined explicitly by two angular coordinates, one indicating the degree of crystal rotation, the other the degree of magnet rotation. Both the crystallographic axes and the spectral axes were plotted on this projection so that the angular relationships between each could be determined graphically. Only a brief description of the manner
in which the stereographic projection and Wulff net were used in this experiment is given.

Briefly, the stereographic projection enables directional properties of crystals to be represented graphically. Crystal axes are represented as points and crystal planes are represented as lines. The Wulff stereographic net is the planar projection of a sphere ruled with longitude and latitude circles. These circles when projected, enable any given point on the stereographic projection to be labelled with two angular coordinates. Graphically, these are the rotations necessary to bring the given point into coincidence with a reference point. Physically, these are the rotations necessary to bring a given axis into coincidence with a reference axis.

An example of the use of the Wulff net in this experiment is given in Fig. 5. The longitudinal axis extends horizontally through the center of the projection. The longitude lines of the net are labelled 0 to 180 degrees indicating the arc of possible crystal rotation. The latitude lines of the net are labelled 90 to 270 degrees indicating the arc of possible magnet rotation. The labelling is arbitrary and the projection from only one hemisphere is used. The possible magnet orientations were labelled to correspond with the angular calibration on the magnet base. The 180 degree latitude line indicates the
Fig. 5. Illustration of the use of the Wulff net. The magnetic field is directed parallel to the b axis when the crystal is rotated about a horizontal axis to the 28 degree position indicated on the crystal rotation indicator and the magnet is rotated about a vertical axis to the 21.2 degree position indicated on the calibrated base. The crosses describe 5 degree intervals in the a-c plane.
position at which the magnetic field is directed perpendicular to the broad face of the cavity. The 90 and 270 degree points indicate the positions at which the magnetic field is directed perpendicular to the narrow face of the cavity. Only one longitude and latitude line is indicated for simplicity. These define the position of the b axis.

The labelling of points is according to the convention: 
(X, M) (crystal rotation coordinate, magnet rotation coordinate).

In practice, the stereographic projection is commonly drawn on a thin sheet of tracing paper placed over the Wulff net with a pivot (thumb-tack) through the center. The projection may then be rotated to any position relative to the net. When three crystallographic axes of a set have been found, the planes are drawn through them by rotating the projection about the pivot so that each pair of axes, in turn, lie on a great circle of the net. The plane is traced on the paper over this great circle. Intervals of equal angle may be marked between these two axes, with the net left in the above position, by checking them off as defined by the latitude lines of equiangular spacing which cut this plane at right angles. Equal intervals of 5 degrees drawn in this manner are shown by the crosses in the a-c plane in Fig. 5. Pivoting the projection back to its original position the coordinates of each cross may be read. The
magnetic field may then be directed along the a-c plane in 5 degree intervals, by orienting the magnetic field, in turn, according to each pair of coordinates. Also, if the positions of only two orthogonal axes are known a third may be found graphically. The two known positions, in turn, are aligned on the 180 degree lateral line and the great circle 90 degrees away is traced on the paper over the great circle on the net below. The intersection of the two great circles drawn in this manner defines the third orthogonal axis.
CHAPTER IV
EXPERIMENTAL PROCEDURE

I. MOUNTING THE CRYSTAL ON THE CAVITY PIN

The biggest disadvantage in using the $TE_{102}$ reflection cavity, in the experimental arrangement shown in Fig. 3, is that the intensities of the resonant absorption lines decrease as $\sin^2 \theta$ where $\theta$ is the angle between the applied magnetic field and the rf magnetic field at the position of the sample inside the cavity. Since, in the $TE_{102}$ mode, the microwave magnetic field lines at the sample position run parallel to the broad face of the cavity, it is important to work with the applied magnetic field as closely normal to the broad face of the cavity as possible in order to obtain signals of sufficient intensity. According to the labelling convention of the Wulff net of Fig. 5, this is equivalent to keeping the magnet as far away from the 90 and 270 positions as possible. To achieve this end, the crystal was mounted on the cavity pin such that the crystallographic axes appeared approximately as those shown in Fig. 5. This particular mounting was obtained by trial and error. This mounting enabled the applied magnetic field to be directed parallel to each axis (crystallographic or spectral), in turn, with the result that the spectra did not differ in intensity by more than about 2 to 1. Throughout the entire
experiment, this mounting did not have to be changed.

II. LOCATING THE CRYSTALLOGRAPHIC AXES

The susceptibility axes arising from the macroscopic effect of each type of magnetic complex coincide with the crystallographic axes in the orthorhombic unit cell (Bowers and Owen 1955). As a result, the magnetic complexes of each type appear equivalent to a magnetic field directed along these crystallographic axes. Experimentally, this means that the corresponding absorption lines, arising from each site of the same type, overlap when the magnetic field is directed along a crystallographic axis. This property was used as an aid in determining the positions of the crystallographic axes with high precision. Following the initial insertion of the crystal into the cavity after the X-ray orientation, the magnet and crystal orientations were adjusted carefully using the rotation mechanism until the absorption lines collapsed to form a reduced spectrum. This was observed on the oscilloscope by connecting its input to the output of the PSD. The precise determination of the positions of the crystallographic axes was a necessary prerequisite for the later measurement of the direction cosines of the spectral axes.
III. LOCATING THE SPECTRAL AXES

Locating the spectral axes was very difficult. A commonly-used procedure is to observe a resonance line on the oscilloscope and to change the crystal and magnet orientations, in turn, until the resonance line experiences a turning point or extremum in magnetic field (Hutton and Troup 1964). The reasons why a resonance line experiences a turning point, to a first approximation, at a spectral axis has been given a theoretical explanation in Chapter I. The position on the Wulff net at which this line occurs for one extreme value of magnetic field is marked as one spectral axis of the site which is responsible for this line. The position on the net, at which this line occurs for another extreme value of magnetic field is marked as another spectral axis. The third spectral axis is drawn in 90 degrees from these two using the properties of the net as described in Chapter II.

Using this procedure, many lines failed to give consistent results. In some cases, the resonance lines disappeared in regions where axes were suspected. In other cases, the resonance lines either varied in field out of the range of the magnet or else could not be followed because of interference from other lines.

Ultimately, the positions of the first set of three
different spectral axes were found by Drs. J.R.W. Thyer and F. Holuj using a k-band spectrometer and visual oscilloscope techniques. The angular relationships between these axes and the crystallographic axes were measured from the Wulff net used in the k-band experiment. Thereupon, the positions of these spectral axes were replotted on the Wulff net used in the x-band experiment (the positioning of the crystallographic axes on the Wulff nets used in the x-band and k-band experiments being different).

The small errors encountered in this transfer process were reduced by carefully checking these transferred positions at x-band. The variation in resonant field value with magnetic field direction for most of the lines was greatest in regions near spectral axes. This made it difficult to revise, with any precision, these transferred positions of the axes by viewing the lines on the oscilloscope. Therefore, the axes were determined accurately by plotting detailed angular variations of the lines through their extreme positions. Three other sets of spectral axes were located approximately using the known symmetry of the crystal. These positions were also checked by plotting detailed angular variations. On account of these refinements, the errors in the positions of the spectral axes are not greater than one degree.
IV. PLOTTING THE ANGULAR VARIATIONS

Briefly, the general procedure involved in plotting the angular variations is to orient the magnetic field at equal intervals parallel to a magnetic plane, and at each orientation, to record the spectrum. The lines belonging to the site under investigation are plotted from each recording in order to obtain a pictorial representation of their anisotropy. By examining the angular variations of the spectrum, the total number of lines belonging to each site can be determined and the spectral axes can be distinguished and correctly identified.

Angular variations of the spectrum were taken along each plane of the first set of spectral axes found. The single resonance of a powder sample of the free radical diphenyl picryl hydrazyl (DPPH) was used as a reference marker. It occurs with the isotropic \( g \) value of 2.0036 to a high degree of accuracy. Recordings of those resonance lines occurring at magnetic fields above DPPH were made using the Baush and Lomb recorder. This was done for the purpose of speed, since the number of lines, high in field, were few, and there was little overlap. Recordings of the resonance lines occurring at magnetic fields below DPPH were made using the Electronics Associates xy plotter. Using the Hall probe and gaussmeter, a good spread in linearly-calibrated magnetic field was obtained on the recordings. This
aided in the determination of certain line positions in regions where lines overlapped one another, and in particular, in regions of overlap of lines containing SHFS. Both sets of angular variations were plotted separately and then scaled down together to form a unified full-range angular plot with a common linear magnetic field calibration.

V. IDENTIFYING THE SPECTRAL AXES

As discussed in Chapter I, the resonances in the orthorhombic crystalline field, $S = 5/2$ case, are most widely separated when the magnetic field is directed parallel to the Z axis. The position of this axis is thus immediately evident from the angular variation plots. The X and Y axes, however, are identified in a manner determined by the strength of the crystal field.

In the weak crystal field case, the X and Y axes are commonly chosen such that the next widely separated resonances define the Y axis, and the least separated resonances define the X axis. This choice insure that the $b_2^0$ and $b_2^2$ coefficients have the same sign (Manoogian et. al. 1965).

In the strong crystal field case, when the transitions occur at values of magnetic field where the energy levels are still purely Kramers doublets, the axes are determined in a different manner. The effective $g$ values of certain lines obtained with the field directed parallel to the tentatively-identified X and Y axes are compared with $g_x^1$ and $g_y^1$ vs. $\eta$. 

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
curves plotted from eq. (10) of Chapter I. For the case of
pure Kramers doublets, the experimentally measured X and Y
effective $g$ values correlate with these curves and result
in the immediate identification of these axes. This is
discussed further in Chapter V. Since, in this case, the
crystal field is of intermediate strength, both procedures
were employed.

Following this, the direction cosines of the spectral
axes were measured from the Wulff net.

VI. MEASURING RESONANT FIELDS

All the absorption lines associated with the first set
of spectral axes were identified from an inspection of the
angular variations. Then, the resonant fields of these
lines were measured using the standard technique of proton
magnetic resonance. In conjunction with the $xy$ plotter, the
magnetic field was increased manually and then stopped where
the plotter pen indicated the center of the line to be
measured. The plotter $x$ input sensitivity was set at a high
value and the dc regulated bias control was adjusted so that
a full-length recording could be obtained over just this
single line to be measured. The recorder pen could then be
positioned at the center of this line with good accuracy.
Next, the magnet was rolled away from about the cavity to
make room for the proton probe. It was inserted as close to
the center of the magnet gap as possible. The frequency of
oscillation of the proton probe was adjusted until the proton magnetic resonance signal could be observed by means of an oscilloscope. A small 60 Hz. modulation current from the mains variac was applied to the large modulation coils about the magnet for this purpose. The oscilloscope x input was, in turn, synchronized by the 60 Hz. mains.

In some cases, the frequency of oscillation of this probe is directly measured by an electronic frequency counter or other measuring device. However, in the course of this experiment, technical difficulties made it advantageous to measure the frequency of oscillation of the probe indirectly. A very stable signal generator was employed, part of whose output was applied to the counter and the rest to a small coil of wire acting as an antenna and placed near the probe in the magnet gap. The frequency of the signal generator was varied until it was equal to the frequency of oscillation of the probe. This was indicated by a frequency beat on an oscilloscope used to observe the output of the probe. Tuning the signal generator to the center of this beat, the frequency of the generator, and hence also the probe, was read from the electronic counter. The resonant field could then be calculated from the well known formula for the proton resonance:  

\[ H \ (kg) = \frac{\text{frequency (Mhz.)}}{4.25759} \]
VII. ANALYSING THE FINE STRUCTURE SPECTRA

The measured resonant fields were used in conjunction with a computer program written for the orthorhombic crystalline field, S = 5/2 case. According to the program, the Hamiltonian matrix of the form given in Table I was exactly diagonalized for approximate values of its parameters and the measured resonant fields. The values of these parameters were changed automatically until a favorable fit was obtained between the predicted necessary quantum energies for transitions at the measured resonant fields and the experimentally incident quantum energy. The computer performed the calculations for a positive absolute sign on b^0_2. Then, when the parameters for a best fit were obtained, the energy levels were calculated automatically. If it should happen that b^0_2 is negative, the order of the energy levels is simply reversed. Therefore, the absolute sign of b^0_2 was determined by subjecting the topaz crystal to liquid helium temperature. Briefly, a double glass dewar was placed about the cavity and part of the waveguide system. Liquid nitrogen was poured into the outer dewar; and liquid helium was poured into the inner dewar next to the cavity. As has been discussed in Chapter I, the lower the temperature of the paramagnetic sample, the greater is the population of those energy levels lying lower in energy. This
means that the intensity ratio of two transitions, say $a/b$, where $a$ is the intensity of a transition between two lower-lying energy levels, and $b$ is the intensity of another transition between two higher-lying energy levels, will increase with decreasing temperature.

Using this argument, it was found that the intensity predictions of the energy level diagrams calculated for positive $b_2^0$ were experimentally reversed. In other words, $b_2^0$ is negative. Thereupon, the energy levels for the magnetic field directed parallel to each spectral axis were plotted for negative $b_2^0$. Then each line of the observed spectra was identified as a specific transition between two energy levels on these plots.
VIII. STUDYING THE SHFS

The following procedure is that which has been used, up to the time of writing, to obtain the SHFS data. This part of the experiment is still in progress.

We must, at this point in the procedure, refer ahead to the angular variation plot in Fig. 7. The variation in the relative splitting of the fine structure line labelled g was studied in the XY and YZ spectral planes; and the relative splitting of the fine structure line labelled a was studied in the XZ plane. This data was obtained using the xy plotter so that recordings were obtained with a linear magnetic field calibration. From the calibrated recordings accurate measurements were made of the relative splitting of the line labelled g at the Y axis, and of the line labelled a at the Z axis. An approximate measurement of the relative splitting of the line labelled b at the X axis was made using the Varian electromagnet with field dial. Since the analysis of the SHFS is still in progress, only a qualitative explanation of this phenomenon is attempted.
CHAPTER V

EXPERIMENTAL RESULTS AND INTERPRETATION

I. THE FINE STRUCTURE

Four sets of differently-oriented but equivalent spectral axes were observed. The positions and identifications of the three axes of each set and their relationships to the crystallographic axes are shown on the stereographic projection in Fig. 6. The evidence for the proper identification of the spectral axes is described below. These four sets of axes are equivalent because the spectra are identical, with the magnetic field parallel to the corresponding axes of each set, and because the four sets are related by symmetry. These facts also indicate the absence of any other spectral axes, and consequently, the absence of any other impurity sites.

The angular variations of the spectra in each of the spectral planes of the set of spectral axes 1 are shown in Fig. 7. The lower case labelling of each line is explained below. Blanks in otherwise smooth curves indicate regions where the lines were not observed. Dotted curves indicate regions where lines were obscured due to overlap from other lines.

By referring to Fig. 7, we may now describe how the spectral axes were properly identified. The Z axis was
Fig. 6. Stereographic projection showing the crystallographic axes and the Fe$^{3+}$ spectral axes in topaz. The Fe$^{3+}$ sites giving rise to these sets of axes are correspondingly labelled with roman numerals in Fig. 4.
Fig. 7. Rotation pattern of the EPR spectra at x-band frequency with H rotated in the quarter spectral planes in topaz.
defined immediately by the most separated resonances. Also, Fig. 7 supplies clear evidence for the identification of the X and Y axes if they can be chosen according to the convention used in the case of weak crystal fields discussed in Chapters I and IV. Initially, in the absence of any other data, the X and Y axes were tentatively-identified using this convention. The measured resonant fields and effective g values of the absorption lines, observed with the magnetic field parallel to the spectral axes identified in this manner, are given in Table II. More evidence for the identification of the X and Y axes was provided by the theory for the case of strong crystal fields. It seemed reasonable to expect that at least those lines occurring at the lower values of magnetic field should represent transitions between energy levels which are of, or very close to, the pure Kramers doublet form. As a consequence, the effective g values of these lines should compare favorably with the corresponding $g_\alpha^1$ vs. $\gamma$ curves calculated from eq. (10) of Chapter I. These curves for $\alpha = X$ and $Y$ are given in Fig. 8. In this figure are plotted the tentatively-identified $g_x$ and $g_y$ values from Table II. Fig. 8 indicates that the effective g value of that line lying lowest in magnetic field, when the field is parallel to the tentative Y axis, fits very well with the $g_y^1$ curve. This means that this line represents almost a pure $M_s = 1/2 \leftrightarrow -1/2$
TABLE II

Resonance fields in kgauss and effective g values of Fe$^{+3}$ EPR fine structure lines in topaz at x-band frequencies.

<table>
<thead>
<tr>
<th>Resonance fields</th>
<th>Effective g values</th>
</tr>
</thead>
<tbody>
<tr>
<td>x 1.699 (b)</td>
<td>3.87</td>
</tr>
<tr>
<td>x 3.68k (g)</td>
<td>1.79</td>
</tr>
<tr>
<td>x 6.128 (a)</td>
<td>1.07</td>
</tr>
<tr>
<td>y 0.703 (g)</td>
<td>9.36</td>
</tr>
<tr>
<td>y 1.883 (b)</td>
<td>3.50</td>
</tr>
<tr>
<td>y 2.561 (h)</td>
<td>2.57</td>
</tr>
<tr>
<td>y 3.752 (i)</td>
<td>1.75</td>
</tr>
<tr>
<td>y 7.106 (j)</td>
<td>0.93</td>
</tr>
<tr>
<td>z 0.669 (a)</td>
<td>9.83</td>
</tr>
<tr>
<td>z 1.393 (b)</td>
<td>4.72</td>
</tr>
<tr>
<td>z 2.479 (c)</td>
<td>2.65</td>
</tr>
<tr>
<td>z 4.061 (d)</td>
<td>1.62</td>
</tr>
<tr>
<td>z 5.257 (e)</td>
<td>1.25</td>
</tr>
<tr>
<td>z 7.962 (f)</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Letters in brackets identify the resonance fields with the angular variations in Fig. 7 and the reproduced recordings of the spectra in Fig. 9.
Fig. 8. The $x$ and $y$ components of the effective $g^1$ tensor as functions of $\eta$. These curves have been calculated assuming $g_a = 2$. The tentatively-identified $g_x$ and $g_y$ values are given by the solid and open circles respectively. They have been plotted for $\eta = 0.434$, the value obtained from the final computer analysis.
transition. No other g value gives such a good fit for any other curve. This evidence proves beyond doubt that the axes are correctly identified.

The above procedure was also used to obtain an estimate of the value of \( \eta \) independent of the computer calculations. With \( \eta \) unknown, the largest effective \( g_x \) and \( g_y \) values were plotted directly on curves of the form given in Fig. 8. These curves showed that \( \eta \) was probably in the range \( 0.35 < \eta < 0.45 \). This is evident from Fig. 8 if \( \eta \) is assumed unknown.

Recordings of typical spectra obtained at room temperature with the magnetic field parallel to the \( X, Y \) and \( Z \) axes of any given site are reproduced in Fig. 9. The lines belonging to this site are labelled by lower case letters. The angular variations of these lines are correspondingly labelled in Fig. 7.

Since there exist four equivalent sets of axes, the experimental results are consistent with a view that the observed spectra are due to a paramagnetic impurity occupying, substitutionally, the octahedral \( \text{Al}^{3+} \) sites. This has been discussed in Chapter III. The four pairs of paramagnetic impurity in the aluminum sites, which are each equivalent due to the center of symmetry located in the center of the cell, are labelled I to IV in Fig. 4. The corresponding sets of spectral axes belonging to these sites are labelled
Fig. 9. The EPR spectrum in topaz at X-band frequency and 290 degrees K. (a), (b), and (c) show the spectra with the applied magnetic field parallel to the X, Y, and Z spectral axes, respectively.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
in the same manner on the stereographic projection in Fig. 6. The assignment of these labels is explained as follows. The set of spectral axes used for all measurements is labelled I. The unit vector parallel to the Z axis of this set was compared with unit vectors parallel to the bond directions of all four pairs of sites. It lay closest to the aluminum-oxygen bond direction a of the pair of sites labelled I in Fig. 4. Because of this fact, it is assumed in the following analysis that the set of spectral axes labelled I arises from the pair of sites labelled I. The pair of sites I, in turn, are equivalent to the pair of sites II due to the mirror planes parallel to the a-b plane. The equivalence of the corresponding sets of axes is illustrated by the same symmetry in Fig. 6, and the set of spectral axes II is labelled accordingly. Also, the pair of sites I are equivalent to the pair of sites III due to a screw axis parallel to the a axis. From the point of view of EPR, and as indicated in Fig. 6, this screw operation is equivalent to a simple 180 degree rotation about the a axis. Thus the set of spectral axes III is correctly labelled.

The set IV follows.

The direction cosines of the set of spectral axes labelled I are given in Table III. The direction cosines of any other axis as projected from the upper hemisphere in Fig. 6, may be found from these values by making the
TABLE III
Direction cosines of the set of spectral axes I

<table>
<thead>
<tr>
<th>Axis</th>
<th>To a</th>
<th>To b</th>
<th>To c</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>0.445</td>
<td>0.881</td>
<td>0.162</td>
</tr>
<tr>
<td>Y</td>
<td>0.792</td>
<td>-0.311</td>
<td>-0.521</td>
</tr>
<tr>
<td>Z</td>
<td>0.402</td>
<td>-0.359</td>
<td>0.843</td>
</tr>
</tbody>
</table>
appropriate sign changes dictated by symmetry.

A stereographic projection showing the orientation of the spectral axes and crystallographic axes through the octahedral impurity site I is given in Fig. 10. It has been constructed from calculations of analytical geometry. This figure may be made to represent the other sites by making the appropriate changes in the directions of the crystallographic axes.

As discussed in Chapter IV, the parameters of the Hamiltonian were calculated by means of the computer, programmed for the $S = \frac{5}{2}$ case. The analysis was carried out by Dr. J.R.W. Thyer. The results of the analysis are given in Table IV. Table V shows the degree of fit of the measured resonant fields with the energy levels predicted by the Hamiltonian incorporating these constants.

The computer calculations were made assuming $b^0_2$ positive. Then, the spectra were observed with the sample at liquid helium temperature in order to determine the absolute sign of $b^0_2$. Recordings of the spectra obtained with topaz at liquid helium temperature are reproduced in Fig. 11. The energy level diagrams calculated for the above parameters, and negative $b^0_2$ are given in Fig. 12. The labelling of each transition on these diagrams is identical to that of Figs. 7 and 9. Clearly, at the lower temperature, those energy levels lying lower in energy have the greater
Fig. 10. Stereographic projection of the Fe$^{+3}$ site I. The equatorial plane of the projection is the plane containing the Fe$^{+3}$ ion and the fluorines. The oxygen ions are indicated by single circles, and the fluorines by double circles. The reference sphere is taken as 1.97 Å in radius. Axes and bond directions have been extended to their intersections with the reference sphere. The heavy solid lines represent spectral axes whereas the heavy dotted lines represent crystallographic axes. Both hemispheres are projected: the light elongations of lines indicate projections from the lower hemisphere.
TABLE IV

Constants of the spin Hamiltonian

<table>
<thead>
<tr>
<th>Constant</th>
<th>For the Fe^{3+} octahedral Al^{3+} site</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_x$</td>
<td>2.0028</td>
</tr>
<tr>
<td>$g_y$</td>
<td>2.0015</td>
</tr>
<tr>
<td>$g_z$</td>
<td>2.0011</td>
</tr>
<tr>
<td>$b_0^0$</td>
<td>-3.445 kg.</td>
</tr>
<tr>
<td>$b_2^0$</td>
<td>-2.594 kg.</td>
</tr>
<tr>
<td>$b_4^0$</td>
<td>0.061 kg.</td>
</tr>
<tr>
<td>$b_2^{1/2}$</td>
<td>0.147 kg.</td>
</tr>
<tr>
<td>$b_4^{1/2}$</td>
<td>0.008 kg.</td>
</tr>
</tbody>
</table>

TABLE V

Errors of fit of measured resonant fields with energy levels

<table>
<thead>
<tr>
<th>Axis</th>
<th>Resonant field (kilogauss)</th>
<th>Error (kilo-electrongauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>1.699(b)</td>
<td>0.008</td>
</tr>
<tr>
<td>X</td>
<td>3.684(g)</td>
<td>-0.044</td>
</tr>
<tr>
<td>X</td>
<td>6.128(a)</td>
<td>-0.024</td>
</tr>
<tr>
<td>Y</td>
<td>0.703(g)</td>
<td>-0.006</td>
</tr>
<tr>
<td>Y</td>
<td>1.883(b)</td>
<td>-0.007</td>
</tr>
<tr>
<td>Y</td>
<td>2.561(h)</td>
<td>-0.018</td>
</tr>
<tr>
<td>Y</td>
<td>3.752(i)</td>
<td>0.021</td>
</tr>
<tr>
<td>Y</td>
<td>7.106(j)</td>
<td>-0.030</td>
</tr>
<tr>
<td>Z</td>
<td>0.669(a)</td>
<td>-0.001</td>
</tr>
<tr>
<td>Z</td>
<td>1.393(b)</td>
<td>0.002</td>
</tr>
<tr>
<td>Z</td>
<td>2.479(c)</td>
<td>-0.012</td>
</tr>
<tr>
<td>Z</td>
<td>4.061(d)</td>
<td>-0.006</td>
</tr>
<tr>
<td>Z</td>
<td>5.257(e)</td>
<td>-0.012</td>
</tr>
<tr>
<td>Z</td>
<td>7.962(f)</td>
<td>-0.018</td>
</tr>
</tbody>
</table>
Fig. 11. The EPR spectrum in topaz at x-band frequency and 4.2 degrees K. (a), (b), and (c) show the spectra with the applied magnetic field parallel to the x, y, and z spectral axes, respectively.
Fig. 12a. Energy level diagram for the magnetic field along the X axis. The electron spin transitions are indicated by vertical lines.
Fig. 12b. Energy level diagram for the magnetic field along the Y axis. The electron spin transitions are indicated by vertical lines.
Fig. 12c. Energy level diagram for the magnetic field along the Z axis. The electron spin transitions are indicated by vertical lines.
populations. Consequently, according to the labelling of the figures, the intensity ratio $I_a/I_r$ should be greater at liquid helium temperature than it is at room temperature. Such is found to be the case. Similar intensity changes shown in Table VI prove conclusively that $b_2^0$ is negative.

II. THE SHFS

All fine structure lines at some orientation of magnetic field show superhyperfine splitting. No two lines show the same magnitude of splitting. Some lines exhibit triplet, quartet, and even quintet splitting. In general, the fine structure lines lying lowest in energy, when the magnetic field is parallel to a spectral axis, possess the greatest magnitude of splitting. Also, to first order, the magnitude of the splitting is symmetrical about the spectral axes. The splitting of the fine structure lines above about 5 kilogauss is, in general, unresolved.

Typical xy plotter recordings of the SHFS have been reproduced in Fig. 13. The b fine structure line, which is not shown, also has an approximate triplet form when the magnetic field is parallel to the X axis. The separation between the central line and the outer lines of this triplet is of the order 29.7 gauss.

The angular variations of the relative splitting of the fine structure lines g and a are presented in Fig. 14. The
<table>
<thead>
<tr>
<th>Axis</th>
<th>Ratio</th>
<th>290° K.</th>
<th>4.2° K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>I_a/I_g</td>
<td>3.40</td>
<td>&gt;&gt;6</td>
</tr>
<tr>
<td>Z</td>
<td>I_a/I_c</td>
<td>0.36</td>
<td>0.79</td>
</tr>
<tr>
<td>Z</td>
<td>I_a/I_f</td>
<td>0.25</td>
<td>0.86</td>
</tr>
</tbody>
</table>
Fig. 13. Typical xy plotter recordings of the SHFS in topaz.
(a) Shows the quartet splitting of the g fine structure line with the magnetic field along the Y axis. (b) Shows the triplet splitting of the a fine structure line with the magnetic field along the Z axis.
Fig. 14. Angular variations of the SHFS splitting. Angular variations of the SHFS splitting of the fine structure lines g and a are shown plotted relative to the mean center of the fine structure line. The mean center of the fine structure line is indicated by the dashed line at relative splitting zero.
magnetic field at the mean center of the fine structure lines was measured every ten degrees from the fine structure angular variation plot of Fig. 7. These measurements are indicated at the top of Fig. 14. Work is still in progress to plot the angular variations of the measurable relative splittings of all other lines, notably line b. This is very difficult due to overlap from other lines. The errors in these measurements, to date, is of the order of 2 - 3 gauss, and effort is now underway to reduce this error.

An interesting phenomenon was observed in the region near the X axis. Fig. 7, shows that the angular variation of the fine structure line a exhibits a 'saddle-point' at the X axis. Fig. 14 shows that in the region 20 degrees away from the X axis this line possesses quintet splitting, and over a very small region, from this preliminary study, what appears to be septet splitting. This splitting quickly collapses to form a single line as the magnetic field is brought parallel to the X axis. However, on the other side of the X axis this line disappears, then reforms a single line, and again the quintet form as the magnetic field is directed away from the axis, but with the difference that these lines are of opposite phase. This change is indicated, through three different orientations of magnetic field, in Fig. 15.
Fig. 15. SHFS splitting of the fine structure line a for three orientations of magnetic field in the region of the X axis.
All fine structure lines do not show perfect symmetry about spectral axes. In particular, line b shows extremes in regions ten degrees away from the axes. Line a disappears at about 5 degrees on one side of the X axis.
VI. DISCUSSION AND CONCLUSION

I. DISCUSSION

The angular variations of the spectra illustrate the difficulties in locating the spectral axes at x-band frequencies. All the lines associated with any given site exhibit absolute extremities only when the magnetic field is parallel to the Z axis of that site. The X axis of any given site could not be located independently of the other axes because, when the magnetic field is rotated through this axis, the angular variations of the lines of the site exhibit 'saddle-points'.

The crystal field at the Fe³⁺ site in topaz can be described as of intermediate strength in that over a substantial portion of the range of applied magnetic field 0 - 20 kg, the strength of the crystal field is not so weak as to conserve the spin quantum number of 5/2 nor so strong to produce the effective spin quantum number of 1/2. In these two extreme cases, as has been discussed in Chapter I, perturbation treatments may be used. However, when electron spin transitions occur in regions where the Zeeman term and the crystal field terms are of the same order of magnitude, as happens in topaz, the absorption lines can be described only through an exact diagonalization of the Hamiltonian matrix using numerical analysis. A perturbation treatment...
could have been applied only in the case had the Zeeman term been made much greater in magnitude than the crystal field terms by applying an incident quantum energy of higher frequency, say from that of the Q band (35 Ghz) or higher.

To obtain a more accurate description of the observed spectra a spin Hamiltonian must be used which includes the odd order spin operator terms: \( \frac{1}{2}, \frac{1}{4}, \frac{3}{4} \). The possible experimental errors in the measurements of the resonant fields are no greater than 3 gauss; and the errors of fit of the measured resonant fields with the computed energy levels given in Table V are not within this error. Also, there is evidence from the rotation patterns in Fig. 7 that not all fine structure lines show exact symmetry about spectral axes, which would be the case if \( b^1_2, b^1_4, b^3_4 \) were negligible.

Work is now in progress to include these odd order terms in a computer program for exact diagonalization. This would, of course, result in a revision of the constants of the spin Hamiltonian.

The necessity for a revision of the constants of the spin Hamiltonian also appears likely from the \( g \) values which were obtained in the first analysis. The \( g_x \) is greater than the free spin value whereas \( g_y \) and \( g_z \) are smaller. No probable errors in these values have as yet been worked out but they are certainly smaller than 0.0005. Watanabe (1957) attributes negative deviation of the \( g \) value from the free
spin value to the admixture of $^4P$-derived wave functions to
the ground state through the spin-orbit coupling; and posi-
tive deviation of the g value from the free spin value
(Watanabe 1964) to covalency. In particular, electron-
transfer to the Fe$^{+3}$ ion through the covalent admixture
between the 3d-orbitals of Fe$^{+3}$ and the orbitals of the sur-
rounding ligands gives rise to positive g-shift whereas the
reverse process gives rise to negative g-shift. This ex-
planation leaves the existence of both positive and nega-
tive g-shifts in the same complex doubtful. We do expect,
however, strong covalency due to the large SHFS splitting.

The distortion in the shape of the fine structure line
a and i at liquid helium temperature with the magnetic field
parallel to the X and Y axes, respectively, is due to power
saturation in the sample. Although a very low power level
was used which was, in turn, decreased in order to reduce
the saturation effect, line a remained saturated down to a
recording signal-to-noise ratio of unity.

No discussion of transition probabilities is given
since it is outside the scope of this work.

It is very difficult to discuss clearly the SHFS with-
out the detailed theory at hand. However, the form of the
SHFS splitting given in Fig. 13 does conform to what is ex-
pected if we limit our study to the region where the effect
of the magnetic field on the energy levels is still much

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
smaller than the effect of the crystal field. Fig. 13 shows that the two F\textsuperscript{19} nuclei appear equivalent to the magnetic field when the field is directed along the Z axis. This is to be expected since at this orientation the magnetic field is nearly normal to the F\textsuperscript{19} - Fe\textsuperscript{3+} - F19 plane shown in Fig. 10. The quintet splitting of this line may be due to 'forbidden transitions' for \( \Delta m_1=\pm 1 \). The subsequent decrease in splitting and disappearance of this line is probably due to cross-over of the energy levels. We can offer no explanation for the phase change of this line.

The existence of the large SHFS splitting necessitates considerable covalent bonding between the Fe\textsuperscript{3+} ion and the F\textsuperscript{19} ions. It is surprising to observe such large SHFS splitting when the crystal field is so strong. We expect a strong crystal field to be set up by ligands whose electrons are mainly localized, and in which case, we would expect the effect of the ligand nuclei to be largely shielded. In part, the large SHFS interaction is probably the result of the close proximity of the Fe\textsuperscript{3+} and F\textsuperscript{19} ions determined by the close-packed structure.

II. CONCLUSION

The EPR spectrum of Fe\textsuperscript{3+} in topaz has been investigated at x-band frequencies at 290° K. and 4.2° K. It has been interpreted on the assumption that Fe\textsuperscript{3+} occupies the eight equivalent Al\textsuperscript{3+} sites in topaz. The small errors
encountered in fitting the measured resonant fields to the calculated energy levels determines this fact beyond doubt. The spectrum shows large SHFS in addition to large zero-field splitting. This indicates the probability that much covalent bonding takes place despite localization of the ligand electrons. More study of the mechanism of the superhyperfine interaction is necessary in order to completely interpret the splittings. The constants of the orthorhombic spin Hamiltonian which fit the spectrum to a good approximation are $g_x = 2.0028$, $g_y = 2.0015$, $g_z = 2.0011$, $b_2^0 = -3.445$ kg., $b_2^2 = -2.594$ kg., $b_4^0 = 0.061$ kg., $b_4^2 = 0.147$ kg., $b_4^4 = 0.008$ kg. The negative sign of $b_2^0$ was determined by studying intensity changes of absorption lines at 4.2°K. To obtain a more accurate description of the spectrum the odd order spin operator terms $0^1$, $0^1$, $0^3$ must be included in the spin Hamiltonian.
ACKNOWLEDGMENTS

The author is indebted to Dr. F. Holuj who suggested this problem, to Dr. J. R. W. Thyer for aid and discussion in this work, and to Dr. A. Manoogian for permission to use Fig. 3.
REFERENCES

THYER, J. R. W., and HOLUJ, F. 1966. EPR of Fe+3 in Al2SiO5 pseudomorphs using a new type of resonant cavity (paper read at the Canadian Association of Physicists Annual Congress, Sherbrooke, Quebec, June 9, 1966).
VITA AUCTORIS


1946 Emigration to Canada.

1956 Graduated from S. S. #1 Public School, Maidstone, Ont.

1961 Graduated from Essex District High School, Essex, Ont.

1965 Bachelor of Science Degree from University of Windsor, Windsor, Ontario.