ELECTRON PARAMAGNETIC RESONANCE STUDIES
OF A NUMBER OF SOLID STATE SYSTEMS

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INTRODUCTION

One of the most valuable tools at the disposal of the solid state investigator at present is the electron spin magnetic resonance method. Electron spin resonance studies have made important contributions to our knowledge of electron interactions in solids and have been useful in determining the nuclear spins of many nuclei. This method can be applied to almost any system which contains unpaired electrons. Atoms or ions fulfilling this condition are those having unfilled shells. Electron spin resonance is therefore observed for atoms or ions which belong to one of the following groups: the (3d) iron group, the (4d) palladium group, the (5d) platinum group, the (4f) rare earth group, and the (5f) uranium group. Other systems which contain unpaired electrons are free radicals, color-center crystals, donor atoms in semi-conductors and conduction electrons in metals. Hence it is apparent that there are large numbers of systems which can be investigated by electron magnetic resonance.

The first successful paramagnetic resonance experiments were performed by Zavoisky\(^1\) and Cummerow and Halliday.\(^2\) In the

\(^1\)E. T. Zavoisky, J. Physics, U.S.S.R. 2, 211 (1945).
Initial experiments several powders of iron group salts were studied. Bleaney and co-workers at Oxford continued the work on polycrystalline salts of the iron group and extended the experiments to the study of single crystals of the undiluted salts. The work on single crystals yielded precise information on the ground state of iron group ions subjected to crystalline electric fields. Application of the resonance method to the study of magnetically dilute crystals led Penrose to discover hyperfine structure in the electron resonance spectrum. Also in 1949 Ingram studied nuclear quadrupole effects on the paramagnetic resonance spectrum of a dilute copper salt. Successful study of the iron group has stimulated a number of workers to investigate, in addition to other iron group salts, many of the other paramagnetic groups in the periodic table. A survey and review of this work is given in articles by Bleaney and Stevens and Bowers and Owen.

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Paramagnetic resonance in substances other than the transition elements or their compounds was first observed by Holden et al.\(^7\) in the organic free radical $\beta$ (phenyl nitrogen oxide)-$\beta$ methyl pentane-$\delta$-one oxime $N$-phenyl ether. Soon thereafter the method was applied successfully to the study of color center crystals by Hutchison,\(^8\) donor atoms in semi-conductors by Fletcher,\(^9\) and conduction electrons in metals by Hutchison and Pastor.\(^{10}\)

The present work is concerned with the application of the electron spin resonance technique to a number of different systems. A major portion of this dissertation is devoted to electron spin resonance measurements on single crystals of $\text{Al}_2\text{O}_3$ containing Cr and Fe as impurities. The purpose of these studies was to investigate the ground state of the $\text{Cr}^{+++}$ and $\text{Fe}^{+++}$ ions in a strong crystalline electric field of trigonal symmetry. Chapters III and IV contain the results of these measurements.
In Chapter V a method of computing the principal components of an asymmetric (g) tensor from paramagnetic resonance data is presented for the case $S = 1/2$. The paramagnetic resonance spectrum of a single crystal of topaz $(Al\,F)_2\,Si\,O_4$ containing Fe and Cr as impurities is discussed in Chapter VI.

Chapter VII is concerned with attempts to determine the valence state of manganese in algae by using electron resonance methods. In addition, the effect of adding acids to water solutions of $Mn\,Cl_2 \cdot 4\,H_2O$ on the $Mn^{++}$ resonance is presented.

Bulk paramagnetic susceptibility and optical measurements on organic phosphors have indicated that the excited metastable state responsible for phosphorescence in these molecules is a triplet state. Described in Chapter VIII are unsuccessful attempts to detect electron spin resonance absorption of the metastable triplet state in a number of organic phosphors at $300^\circ K$ and $80^\circ K$.

In Chapter IX the electron resonance spectra of free radicals produced by X-ray and $\beta -$irradiation of carbohydrates are presented. The results indicate that for a given sugar the free radical formed does not depend on whether the damaging radiation is X-ray or $\beta -$irradiation. Similarities in the hyperfine structure of radicals in several different sugars are noted.
CHAPTER I

THEORY

The Resonance Condition

The paramagnetic resonance phenomenon is realized in a simple form when one considers a free ion with angular momentum $\mathbf{J}$ and magnetic moment $-g_J \beta \mathbf{J}$ in a magnetic field $\mathbf{H}$. The ion has energies of orientation in the magnetic field equal to $M_J g_J \beta H$, where $M_J$ is the magnetic quantum number of the ion, $\beta$ is the Bohr magneton and $g_J$ is the Landé splitting factor. Magnetic dipole transitions between these levels are allowed under the selection rule $\Delta M_J = \pm 1$. Such magnetic dipole transitions can be induced between the energy levels by applying an oscillating magnetic field of frequency $\nu = (g_J \beta H/h)$ perpendicular to $\mathbf{H}$. When the ions are in thermal equilibrium, there are more ions in the lower energy states; hence, a net absorption of power at frequency $\nu$ occurs.

The absorption of power can be measured in a paramagnetic resonance experiment by placing the sample in a resonant wave guide cavity and observing the change in transmitted power at resonance. From the standpoint of convenience one normally fixes the frequency $\nu$ and varies the field $H$ until the resonance condition is satisfied; i.e., $H = (h \nu / g_J \beta)$. For the case of the free ion
considered, there occurs only a single absorption line since all the transitions coincide.

In general the spectrum of a paramagnetic ion in a crystal is more complex. The lowest energy levels between which transitions are induced depend in a rather complicated manner on the ion, on the crystalline electric field and on the spin-orbit coupling. Additional complications arise because of the interaction of the magnetic moment of the electrons with the magnetic moment of the nucleus. In the interpretation of paramagnetic resonance experiments, however, it is customary to fit experimental data to a spin Hamiltonian. The use of a spin Hamiltonian for the description of the lowest group of spin states in the ion allows one to interpret the resonance properties of the paramagnetic material in terms of a relatively small number of constants. The constants in the spin Hamiltonian are generally not specified but are related to fundamental properties of the solid; namely, the electron configuration of the ion, the crystalline electric field and the spin-orbit coupling.

For paramagnetic ions in solids the spin Hamiltonian can be derived from first principles. Bleaney and Stevens\textsuperscript{5} have presented a derivation of the spin Hamiltonian for ions in the iron group. The salient features of such a derivation and a discussion of the terms appearing in the spin Hamiltonian are given in the remainder of this chapter.
Hamiltonian of a Paramagnetic Ion

The total Hamiltonian for a paramagnetic ion in a solid has been given by Abragam and Pryce.\textsuperscript{11} We shall consider here only those terms which are important for the interpretation of spectra presented in this dissertation. The relevant terms of the Hamiltonian follow:

1. The Coulomb interaction of the electrons with the nucleus and with each other is given by

\[
\sum_{\kappa} \left( \frac{p_{\kappa}^2}{2m} - \frac{Z e^2}{\kappa \kappa} \right) + \sum_{j<k} \frac{e^2}{\kappa j k} .
\]  

(1.1)

Energy separations produced by this term are of the order of $10^5$ cm\(^{-1}\).

2. One form of the magnetic interaction of the electron spins and the orbits is given by

\[
\sum_{j \kappa} \left\{ a_{jk} \mathbf{d}_j \cdot \mathbf{s}_k + b_{jk} \mathbf{l}_j \cdot \mathbf{l}_k + c_{jk} \mathbf{s}_j \cdot \mathbf{s}_k \right\} .
\]

(1.2)

The spin-orbit coupling term produces energy separations of approximately $10^2$ cm\(^{-1}\), whereas the spin-spin interaction is approximately 1 cm\(^{-1}\).

3. An external magnetic field produces the interaction which is given by

\[
\sum_{\kappa} \left( \frac{e}{4\pi mc} \right) \left( \mathbf{L}_\kappa + 2 \mathbf{S}_\kappa \right) \cdot \mathbf{H} .
\]

(1.3)
Magnetic fields of the order of 10,000 gauss produce splittings of approximately 1 cm$^{-1}$.

4. Using Dirac theory, Fermi$^{12}$ has derived the form of the interaction of the magnetic moment of the nucleus with the magnetic field produced by the electron cloud. The interaction has the form

$$2 g_I \beta_n \sum_k \left\{ \left( \frac{I_k - s_k}{r_k^3} \right) \cdot \mathbf{I} + 3 \left( \frac{r_k \cdot s_k}{r_k^5} \right) (r_k \cdot \mathbf{I}) \right\} + \frac{8\pi}{3} \delta(r_k) (s_k \cdot \mathbf{I}) \right].$$

(1.4)

Here the energy of interaction is approximately $10^{-2}$ cm$^{-1}$.

5. The influence of the crystalline electric field on the paramagnetic ion gives rise to the interaction

$$\sum_k \left[ -e V(x_k, y_k, z_k) \right]$$

(1.5)

where $V(x_k, y_k, z_k)$ is the crystalline field potential at the $k$th electron. For ions in the iron group the energy of interaction is approximately $10^4$ cm$^{-1}$.

The terms which have been neglected are the interaction between the electrons and the nuclear quadrupole moment and the interaction of the nuclear magnetic moment with the external magnetic field.
For ions in the iron group the crystalline electric field effect is small compared with the coulomb energies but large compared with the spin-orbit interaction. As a first approximation the terms in (1.1) and the last two terms in (1.2) are treated by methods described in Condon and Shortley.\textsuperscript{13}


Such a treatment gives energy states for the ion which are specified by the electron configuration and the total orbital and spin angular momentum of the ion; for example, \(1\,s^2\,2\,s^2\,2\,p^6\,3\,s^2\,3\,p^6\,3d^3\), \(4F\). The next step is to consider how the crystalline electric field affects the ground-state orbital levels of the ion; for the present the spin-orbit coupling term will be neglected.

\textbf{The Crystal Field}

Bethe,\textsuperscript{14} Becquerel and Opechowski,\textsuperscript{15} Abragam and Pryce,\textsuperscript{11} and Stevens,\textsuperscript{16} have treated the effect of the crystalline electric field on the ground-state orbital


\textsuperscript{15}J. Becquerel and W. Opechowski, Physica. 6, 1039 (1939).

levels. In the treatment it is assumed that the potential satisfies Laplace's equation and can be expanded in spherical harmonics.

\[ \nabla (r, \theta, \phi) = \sum_{m} \sum_{n} a_{m}^{n} r^{n} Y_{n}^{m}(\theta, \phi) \quad (1.6) \]

Here \( Y_{n}^{m}(\theta, \phi) \) is a normalized spherical harmonic. In the expansion \( A_{n}^{m} = (A_{n}^{-m})^{*} \); this is just the condition that the potential be real. At this point the polar axis used to describe the crystal field is chosen as the axis of quantization for the wave functions \( Y_{L, S}^{M_{L}, M_{S}} \) of the ground state, where \( M_{L} \) denotes the component of angular momentum \( L \) in the direction of the polar axis. \( M_{S} \) denotes the component of spin angular momentum \( S \) in the direction of the polar axis. It is necessary to consider the following matrix elements

\[ \int (\psi_{L, S}^{M_{L}, M_{S}})^{*} \left\{ \sum_{k} e^{i V(r_{k}, \theta_{k}, \phi_{k})} \right\} (\psi_{L, S}^{M'_{L}, M'_{S}}) d \tau \quad (1.7) \]

in the secular determinant. The evaluation of these matrix elements can be carried out, since the \( Y_{L, S}^{M_{L}, M_{S}} \) are states formed by taking linear combinations of antisymmetrized product states in an \( l_{z}, s_{z} \) representation. For a given \( M_{L} \) and \( M_{S} \) the particular linear combination is determined by the vector addition rules given in Condon and Shortley.\(^{13} \)
When this is done the secular determinant of (1.7) has the form

\[
\begin{vmatrix}
C + U_{M_L, M_L} - \lambda & D_{M_{L'}, M_{L'}} & \cdots \\
D_{M_{L'}, M_{L'}} & C + U_{M_{L'}, M_{L'}} - \lambda & \cdots \\
\cdots & \cdots & \cdots
\end{vmatrix} = 0. (1.8)
\]

Here \(C\) is the sum of matrix elements due to closed shell electrons. The \(U_{M_L, M_L}\) and the \(D_{M_{L'}, M_{L'}}\) are the sum of matrix elements due to the electrons in unfilled shells. Inspection of (1.8) shows that the interaction of the crystal field with the closed-shell electrons simply raises the energy of each \(M_L\) level in the ground state by an amount \(C\) and does not have an effect in removing the orbital degeneracy of the ground state.

The number of terms that need to be considered in (1.6) can be reduced, since \(U_{M_{L'}, M_L}\) and \(D_{M_{L'}, M_{L'}}\) contain only matrix elements of the unfilled shell electrons which for the iron group are the 3d electrons. For the 3d electrons the only non-zero matrix elements come from the terms in (1.6) for which \(n\) is even and less than or equal to 4. One usually drops the term with \(n = 0\), since it contributes only an additive constant to the energy of the ground state.
Evaluation of \( U_{M_L, M_L} \) and \( D_{M_L, M_L} \), by using for
\( \psi_{L, S}^{M_L, M_S} \) the product of one electron states, is rather laborious and Stevens\(^{16}\) has shown that the matrix elements of the crystal field are proportional to matrix elements of certain linear combinations of the total orbital angular momentum operators \( L_x, L_y \) and \( L_z \); for example,

\[
\sum_k r_k^2 Y_2^0(\Theta_k, \Phi_k) = \alpha \overline{r^2} \left\{ 3L_z^2 - L(L+1) \right\}
\]

\[
\sum_k r_k^4 Y_4^0(\Theta_k, \Phi_k) = \beta \overline{r^4} \left\{ 35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2 \right\}
\]

where \( \alpha \) and \( \beta \) are known constants and \( \overline{r^2} \) is the radial average of \( r^2 \) for a 3d electron. In this manner one can solve (1.8) to find the lowest orbital state. Having dealt with the effect of the crystal field, one now finds it necessary to consider how perturbations due to the first term in (1.2) and the terms in (1.3) and (1.4) affect this lowest state. It is assumed that the lowest state is an orbital singlet with a \((2S + 1)\) - fold spin degeneracy.

**The Spin Hamiltonian**

The first term in (1.2) and the terms in (1.3) and (1.4) can be reduced to expressions containing the total orbital angular momentum \( L \) and the spin angular momentum \( S \) of the ion. The procedure is very similar to that which was carried out for the crystal field. If this is done
then these terms have the form

\[ \sum_{j_k} a_{j_k} L_j \cdot S_k = \lambda (\mathbf{L} \cdot \mathbf{S}) \]

\[ \sum_{k} \left( \frac{e \hbar}{4 \pi mc} \right) \left( \ell_k + 2 s_k \right) \cdot \mathbf{H} = \beta (\mathbf{L} + 2 \mathbf{S}) \cdot \mathbf{H} \]

(1.9)

and (1.4) is

\[ \left( \frac{r}{\hbar} \right)^2 \beta \beta_n \left[ L + \frac{1}{4} \left\{ \mathbf{L} (\mathbf{L} + 1) (\mathbf{S} \cdot \mathbf{I}) - \frac{1}{2} \mathbf{L} \cdot \mathbf{S} (\mathbf{L} \cdot \mathbf{I}) - \frac{3}{2} (\mathbf{L} \cdot \mathbf{I}) (\mathbf{S} \cdot \mathbf{I}) \right\} \right. \]

\[ - \kappa (\mathbf{S} \cdot \mathbf{I}) \]

Even though it was assumed that the lowest energy state is an orbital singlet, the state is degenerate with respect to the spin. In order to take into account the perturbation of (1.9), it is necessary to use degenerate perturbation theory on this lowest state. Fortunately, however, Pryce\textsuperscript{17} has derived a much simpler method which


is equivalent to degenerate perturbation theory. This approach leads to the important spin Hamiltonian concept. In the method the electron spin \( \mathbf{S} \) and the nuclear spin \( \mathbf{I} \) are treated as non-commuting algebraic quantities. Hence instead of obtaining the perturbed energies, an expression which involves the components of \( \mathbf{S} \) and \( \mathbf{I} \) is obtained. The actual energies of the ground state are the eigenvalues of this new operator known as the spin Hamiltonian.
To illustrate how the method proceeds, let us consider a simpler perturbation than (1.9). Consider the perturbation

$$\hat{H}' = \beta H \cdot (L+2S) + \lambda (L \cdot S) + A(I \cdot S) \quad (1.10)$$

In the Dirac notation, the ground orbital state is indicated as $|0\rangle$ and the excited states as $|n\rangle$, with energies $E_n$ where $n = 0, 1, 2, 3$ etc.. In first order one has

$$<0|\hat{H}'|0> = <0|\beta H \cdot (L+2S) + \lambda (L \cdot S) + A(I \cdot S)|0>. \quad (1.11)$$

For the terms $<0|2\beta H \cdot S|0>$ and $<0|A(I \cdot S)|0>$ there are no operators acting on the orbits; hence, they give $2 \beta H \cdot S + A(I \cdot S)$. The contribution in first order is zero for the term $<0|\beta H \cdot L + \lambda (L \cdot S)|0>$ because an orbital singlet state has no orbital moment; i.e.

$$<0|L_x|0> = <0|L_y|0> = <0|L_z|0> = 0.$$  

The contribution in second order is given by

$$-\sum_{\lambda \neq 0} \frac{|<0|\beta H \cdot (L+2S) + \lambda (L \cdot S) + A(I \cdot S)|n>|^2}{E_n - E_0}. \quad (1.12)$$

In (1.12) the terms which do not involve orbital variables vanish since $<0|n> = 0$ for $n \neq 0$. Upon expansion (1.12) takes the form

$$-\beta^2 \Lambda_{ij} H_i H_j + (-2\beta \lambda \Lambda_{ij}) S_i H_j - \lambda^2 \Lambda_{ij} S_i S_j \quad (1.13)$$
where

\[ \mathcal{J}_{ij} = \sum_{n \neq 0} \frac{\langle \text{coll} \mid i \text{to} \rangle \langle n \mid i \text{to} \rangle}{E_n - E_0}. \]

Collecting the contributions from (1.11) and (1.12), one has that the spin Hamiltonian, correct to second order for the perturbation (1.10), is

\[ \mathcal{H}_S = 2\beta (\xi_j - \lambda m_j) S_i \cdot \mathbf{H}_j - \lambda^2 \mathbf{S}_i \cdot \mathbf{S}_j - \mathbf{H}_i \cdot \mathbf{H}_j + A \mathbf{I} \cdot \mathbf{S} \quad (1.14) \]

where \( \xi_{1j} = 1 \) for \( i = j \) and \( \xi_{1j} = 0 \) for \( i \neq j \). If one had used all the terms in (1.9) as the perturbation to the ground orbital state, an additional term \( A_{ij} \mathbf{I}_i \mathbf{S}_j \) would have appeared in the spin Hamiltonian. The treatment above was restricted to the case where the lowest orbital state produced by the crystal field was a singlet. When the lowest energy state is orbitally degenerate, the derivation of the spin Hamiltonian is more difficult. In addition, the treatment given above does not apply to \( S \) state ions (\( L = 0 \)) in the iron group. Fig. 1 illustrates the effect of the various perturbations on the ground state of the free ion.

**Discussion of Terms in the Spin Hamiltonian**

Before discussing the terms in the spin Hamiltonian, it is convenient to write (1.14) in the more common form

\[ \mathcal{H}_S = \beta g_j \mathbf{I}_i \mathbf{S}_j + \xi_j \mathbf{S}_i \cdot \mathbf{S}_j + A_{ij} \mathbf{I}_i \mathbf{S}_j - \beta^2 \mathbf{S}_i \cdot \mathbf{S}_j \quad (1.15) \]
Since the term $-\beta^2 \Lambda_{ij} H_i H_j$ does not contain $S$ or $I$, it appears as an additive constant in the energy. Hence it is usually neglected in the discussion of experimental resonance data. For simplicity in discussing the terms which appear in the spin Hamiltonian, it is convenient to assume that the symmetry of the crystal field is trigonal. In the discussion the $z$-direction is chosen parallel to the axis of symmetry of the field. Since the spin Hamiltonian must exhibit the same symmetry as the crystal field, it takes the form

$$H_S = \beta \left[ g_{ii} H_z S_z + g_{il} (H_x S_x + H_y S_y) \right] + D S_z^2 + A S_z I_z + B (S_x I_x + S_y I_y) \quad (1.16)$$

where

$$g_{ii} = 2 (1 - \lambda \Lambda_{zz})$$
$$g_{il} = 2 (1 - \lambda \Lambda_{xx})$$
$$D = \lambda^2 (\Lambda_{xx} - \Lambda_{zz})$$

and $A$ and $B$ are similar but more complicated expressions.
Figure 1

An illustration of the lowest levels of a paramagnetic ion in a crystalline electric field of trigonal symmetry is given. The splitting of a $^4F$ state is shown for a trigonal field containing only $\gamma_{3/4}^{-3}$ and $\gamma_{3/4}^{3}$ terms in the potential. The total degeneracy (spin plus orbit) of each level is shown in parentheses. The splittings due to spin-orbit coupling and the applied magnetic field are greatly exaggerated. The paramagnetic resonance spectrum arises from transitions between the levels shown on the extreme right.
Free Ion  Trigonal Field  Spin-Orbit Coupling  Effect of Magnetic Field Applied Parallel to Trigonal Axis
The spectroscopic splitting factor $g$.—It is recalled that for the case of the resonance spectrum of a free ion the resonance condition is $h\nu = g_\perp \beta H$, where $g_\perp$ is the Landé splitting factor. For a paramagnetic ion in a crystal, a spectroscopic splitting factor $g = \frac{h\nu}{\beta H}$ is defined in a similar manner. However in this case $g$ is no longer a simple quantity and it depends on the ion, the crystal, and the spin-orbit coupling parameter $\lambda$. In addition, $g$ is a function of the relative orientation of the crystal and the magnetic field. To see that this is true let us consider only the first term in (1.16)

$$\beta [g_\parallel H_\parallel^2 S_\parallel^2 + g_\perp (H_x^2 S_x^2 + H_y^2 S_y^2)].$$

If $H$ is parallel to the $z$ direction, the eigenvalues of energy are given by

$$E_m = \beta g_\parallel HM_z$$

and the resonance condition is

$$g = g_\parallel = \frac{h\nu}{\beta H}.$$

Whereas if $H$ is in the $xy$ plane, one obtains

$$E_m = \beta g_\perp HM_x$$

and

$$g = g_\perp = \frac{h\nu}{\beta H}.$$

Thus the magnetic moment exhibited by the ion is
anisotropic. If $H$ makes an angle $\Theta$ with the $z$ direction $g$ is given by

$$g^2 = g_{||}^2 \cos^2 \Theta + g_\perp^2 \sin^2 \Theta .$$  \hspace{1cm} (1.17)

Hence the field at which resonance occurs varies as the crystal is rotated with respect to the magnetic field.

**Fine structure.**—Let us now consider the combined effect of the first two terms in (1.16) and discuss their effect on the paramagnetic resonance spectrum. For the case $S=1/2$, the term $D S_z^2$ has no effect on the resonance spectrum. It only produces a splitting of the spin levels in zero magnetic field when $S > 1/2$. Consider the case $S = 3/2$ with $H$ in the $z$-direction. The energy levels are given by

$$E_{3/2} = \frac{3}{2} \beta g_{||} H + \frac{9}{4} D$$

$$E_{1/2} = \frac{1}{2} \beta g_{||} H + \frac{1}{4} D$$

$$E_{-1/2} = -\frac{1}{2} \beta g_{||} H + \frac{1}{4} D$$

$$E_{-3/2} = -\frac{3}{2} \beta g_{||} H + \frac{9}{4} D .$$  \hspace{1cm} (1.18)

Since the selection rules for magnetic dipole transitions in this case are $\Delta M_\sigma = \pm 1$, one has

$$\hbar \nu (1/2 \rightarrow 3/2) = \beta g_{||} H + 2D$$

$$\hbar \nu (-1/2 \rightarrow 1/2) = \beta g_{||} H$$

$$\hbar \nu (-3/2 \rightarrow -1/2) = \beta g_{||} H - 2D .$$
Instead of one line as before, the spectrum consists of three lines separated by $2D$. In the usual paramagnetic resonance experiment, $\nu$ is fixed and $H$ is varied; therefore, the number of lines observed in an experiment depends on the relative magnitude of $D$ and $\nu$ and the range over which $H$ is varied. The intensities of all the lines will not be equal but will depend on the square of the matrix elements $S_+$ and $S_-$ where $S_+ = S_x + iS_y$. In the case cited, the $\nu (-1/2 \rightarrow 1/2)$ transition has an intensity $4/3$ the intensity of the $\nu (1/2 \rightarrow 3/2)$ and the $\nu (-3/2 \rightarrow 1/2)$ transitions. If $H$ is applied at some angle $\theta$ with respect to the symmetry axis of the crystal, one can no longer write down simple energy expressions. As the crystal is rotated the lines will in general move with respect to each other. If $H$ is not parallel to the $z$ direction, each level is a linear combination of the zero field states, and under these circumstances "double jumps" ($\Delta M_S = \pm 2$) are possible.

**Hyperfine structure.**—The effect due to the interaction of the nucleus with the electron spin was shown to give rise to the term $A_{ij} I_i S_j$ in the spin Hamiltonian. Since the nucleus has $2I + 1$ orientations in the magnetic field produced by the $2S + 1$ orientations of the electron spin, each spin level is subdivided into $2I + 1$ components. If the magnetic field is strong, the spacings between adjacent components are equal.
Again for simplicity of illustration, a spin Hamiltonian of the following form

$$\mathcal{H}_s = g \beta H \cdot S + A \cdot S$$  \hspace{1cm} (1.19)

is assumed with $H$ parallel to the $z$ direction and $g \beta H \gg A$. In this case, to first order, the energy levels are given by

$$E_{M_s, M_I} = g \beta H M_s + AM_I M_I, \quad M_I = I, I-1, \ldots, -I.$$  

For magnetic dipole transitions the selection rules are

$\Delta M_s = \pm 1$ and $\Delta M_I = 0$. Hence transitions will occur at values of $H$ such that $\hbar \nu = g \beta H + AM_I$. In the paramagnetic resonance spectrum there are $2I + 1$ lines with equal spacing $A$. For the more general spin Hamiltonian with $A \cdot I \cdot S + A \cdot I \cdot S + A \cdot I \cdot S$, the spacings between the lines vary as the crystal is rotated with respect to the magnetic field.
CHAPTER II

THE ELECTRON PARAMAGNETIC RESONANCE SPECTROMETER

A block diagram of the paramagnetic resonance spectrometer used in the measurements which are reported in this dissertation is shown in Fig. 2.

In a paramagnetic resonance experiment observations are made on transitions between Zeeman levels; therefore, it is necessary to impose a large magnetic field \( H \) on the sample while it is being irradiated with microwave power. In the spectrograph employed the microwave frequency is fixed while the external magnetic field is varied through the absorption line.

A small alternating magnetic field of low frequency is superimposed on the large field \( H \), by use of modulation coils, so as to modulate the intensity of the microwave power in the region of resonance. The amplitude of modulation of the microwave power at the output of the cavity is proportional to the slope of the resonance curve, and the phase will be either in phase or \( 180^\circ \) out of phase with the field modulation signal depending on whether the slope is increasing or decreasing. The signal from the crystal detector at the cavity output is passed through a narrow-band amplifier and into a phase detector. The phase detector provides a d. c. output whose magnitude is
Figure 2

A block diagram of the paramagnetic resonance spectrometer is shown.
proportional to the a.c. input amplitude; its sign depends on whether the input signal is in or out of phase with the reference signal, which is supplied by the field modulation oscillator. If the d. c. output of the phase detector is recorded on a chart recorder as the magnetic field is varied through an absorption line, the first derivative of the absorption line will be traced out. The spectrometer was capable of detecting $10^{13}$ to $10^{14}$ electron spins, provided the width of the absorption line was approximately one to three gauss.

**Klystron and Klystron Stabilizer**

A 723 AB reflex klystron was used as a source of microwave radiation. The frequency range over which the klystron operated was 8700 - 9500 Mc/sec. To reduce frequency drift of the klystron due to temperature changes, the klystron was thermally lagged by placing it in an oil bath. Additional frequency stabilization of the klystron was achieved by a method which is illustrated in Fig. 3. In this system the r.f. beat between the klystron and a suitable harmonic of the secondary frequency standard is fed into a National HRO-50T1 radio receiver which employs a narrow-band (6 kc/sec wide) f.m. discriminator having a response curve with a slope of 0.22 V/kc. at center frequency. The output voltage of the discriminator is then applied to the grid of the d. c. amplifier which supplies the reflector voltage of the klystron. In this way
(a) A block diagram of the klystron frequency stabilizer is shown.

(b) A schematic of the d. c. amplifier is shown.
(a) Block Diagram of Klystron Stabilizer

(b) Schematic of D. C. Amplifier
frequency drift of the klystron relative to the secondary standard is sensed and compensated. In order to operate the output of the f.m. discriminator at -510 V d.c., it was necessary to make some minor modifications to the discriminator; however, these modifications did not alter the normal operation of the HRO-50. The particular d. c. amplifier which was used had a d. c. voltage gain of $30 - 50$ over the range of reflector voltages (135 - 185 V) available by adjustment of $R_1$. It was found necessary for best operation to supply the heaters in the f.m. discriminator and the d. c. amplifier from batteries. All voltages except the reflector voltage were supplied to the klystron by a TVN7 Browning Laboratories power supply.

This klystron stabilizer system was very simple to operate and a warm up period of about a half hour was sufficient for stable operation. The short time stability was comparable with the Pound system in that $\pm 100\text{c.p.s.}$ modulation of the klystron was observed at the power supply ripple frequency. The long time stability was observed to be one part in $10^7$ over a period of several hours, which is the order of drift of the 5 Mc./sec crystal standard.

**Microwave Components**

Standard X-band wave guide components were used in the apparatus. Isolation of the klystron from the rest of
the waveguide system was accomplished by using a Cascade Research Corporation "Uniline" ferrite isolator with a forward loss of 1 db. and a reverse loss of 20 db. A small amount of the energy from the klystron was coupled out of the main wave guide system by means of a forward directional coupler. In the low energy arm of the directional coupler the energy was further divided by a wave guide T section. One of the arms of the T was terminated with a crystal detector which acted as a mixer and provided the r.f. beat between the frequency standard and the klystron. The third arm of the T contained an Auto Ordinance Model 21, reaction type wavemeter. The wavemeter located the frequency of the klystron to within 5 Mc./sec. A slotted line matching section which was equipped with an adjustable probe followed the directional coupler. By proper adjustment of the probe, reflections in the system were minimized. Two "flap attenuators" which were located in front of the sample cavity were used to reduce the microwave power, incident on the cavity, to the desired level.

Two microwave cavities were employed in the paramagnetic resonance experiments. The cavity which was used in the work described in Chapters VII, VIII and IX is shown in Fig. 4. The cavity was resonant at approximately 9300 Mc./sec. and had a Q of 5000.
Single crystal experiments were conducted with the cavity shown in Fig. 5. The cavity section was machined from a brass block and fabricated such that the axis of the divided circle was perpendicular to the sides which contained the modulation coils. The portion of the assembly which constituted the microwave cavity was silverplated. The bottom of the cavity was removable so that the quartz rod on which the single crystal was mounted could be introduced into the cavity. By clamping the pole faces of the magnet against opposite external walls of the cavity, the axis of rotation of the graduated circle was made perpendicular to the magnetic field. The graduated circle which was used to rotate the crystal could be read to 1/4°.

Following the sample cavity was the crystal detector which was used for rectifying the microwave power. Type 1N23B silicon diodes were used in all of the detector mounts.

**Recording Apparatus**

The output of the crystal detector was transformer-coupled to the input of a Ballantine Electronic Voltmeter which was used as a wide-band amplifier. This amplifier operated from self-contained batteries and gave a voltage gain of 1000 with the introduction of very little noise.

The output voltage of the wide-band amplifier was applied to the input of a Model 760A General Radio sound analyzer which was used as a narrow-band amplifier tuned
The sample cavity used for measurements made in Chapters VII, VIII and IX is shown. The cavity was resonant at 9300 Ma/sec. in the TE$_{102}$ mode.
Plastic Form to Hold Mod. Coils in Place

Sample Tube

Hole to Introduce Sample Into Cavity

Coupling Iris to Cavity

$TE_{102}$ Rectangular Cavity

Cable From Power Amp.

Modulation Coils

X-Band Wave Guide
Figure 5

The cavity used for single crystal measurements is shown.
Graduated Circle

Power Cable for Modulation Coils

Glass Platform on Which Crystal is Held

Coupling Iris

Modulation Coils Embedded in Cavity Walls

Removable Plate

X-Band Wave Guide

Cavity Used For Single Crystal Studies
to the field modulation frequency of 800 c.p.s. The sound analyzer had a maximum gain of approximately 10,000.

Following the narrow-band amplifier was the phase-sensitive detector which consisted of a preamplifier, with phase adjustment and a Cox lock-in-amplifier.\textsuperscript{19} The reference phase for the detector was supplied by the field-modulation oscillator.

The d.c. output of the phase detector was applied to an Esterline-Angus 1-milliampere chart recorder which was adjusted to give zero deflection for zero input voltage. When a signal was introduced into the recording system, positive and negative deflections, corresponding to the derivative of the resonance curve, were obtained.

**Magnet Power Supply**

The external magnetic field was produced by an electromagnet. A field of approximately 3000 gauss could be obtained by passing 5 amperes through the magnet field coils. A Tabtron low-voltage power supply was used for this purpose. This unit was a well-filtered selenium rectifier supply and when used with the magnet it was sufficiently stable for the experiments. Coarse control of the magnet current was obtained by use of a variac in the Tabtron supply. The magnet power supply was operated from a Sorenson line voltage regulator. It was possible to

achieve fine control of the magnet current by a method which is shown in Fig. 6. The method consisted of changing the grid voltage on the 6L6GA in the Sorenson and thereby varying the current in the field coil of the saturable reactor which in turn changed the amplitude of the a.c. voltage available to the magnet power supply. The characteristics of this method of slowly varying the magnetic field are shown in Fig. 7. A synchronous motor was used to drive the Helipot dial when absorption spectra were recorded.

**Field Modulation Equipment**

As was indicated in Figures 4 and 5, the magnetic field modulation was produced by small coils mounted on the sides of the microwave cavity. The modulation coils were driven by a power amplifier which in turn was supplied by a Hewlett Packard 200C audio oscillator. The modulation frequency was 800 c.p.s. For best operation the modulation coils were series resonated with 15 uf. The modulation coils were connected in parallel and it was possible to attain modulation amplitudes of 0 - 50 gauss.

**Secondary Frequency Standard**

The secondary frequency standard, which was used in both stabilizing the klystron and in accurately measuring the klystron frequency, was designed and built by Wolfe.

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Figure 6

A schematic diagram of a Sorenson line voltage regulator 1000S is shown. The portion of the figure enclosed by the dashed lines contains the potentiometer which is used in conjunction with the Sorenson to achieve fine control of the magnet current.

The Sorenson 1000S instruction manual gives details about the components in the line voltage regulator.
Output to Magnet Supply
Input to Sorenson
Saturable Reactor
Auto Transformer

6L6GA

470K

90V

15 Turn 100K-5W Helipot
Figure 7
A typical characteristic curve of the fine control variation of the magnetic field is shown.
The essential part of the standard was a temperature controlled 5 Mc./sec. quartz-crystal-controlled oscillator which was adjusted to zero beat with the 5 Mc./sec. signal of WWV. A series of multiplier stages multiplied the 5 Mc./sec. signal to 360 Mc./sec. The 360 Mc./sec. signal which contained 20 Mc./sec. side bands was fed to the crystal detector in the low energy arm of the directional coupler. The crystal detector acted as a multiplier and mixer, and provided a beat frequency between the klystron and the harmonic of the frequency standard. The klystron frequency was an integral multiple of 20 Mc./sec. plus or minus the beat frequency. Identification of the multiple of 20 Mc./sec. was made by measuring the klystron frequency with the cavity wavemeter described previously. By tuning the frequency of the klystron slightly, a determination of whether the klystron was above or below the 20 Mc./sec. marker could be made. By measuring the beat signal of the klystron with one of the 20 Mc./sec. markers on the H.R.O. -50 radio receiver, the klystron frequency was determined to within ± 0.1 Mc./sec.

Measurement of the Magnetic Field

The magnetic field was measured with a nuclear resonance magnetometer. Measurement of the magnetic field was accomplished by observing at what frequency nuclear magnetic resonance occurs for either a proton sample or a sample containing Li^7 nuclei. A type BC-221-T frequency meter was used to measure this frequency.
The magnetometer probe was positioned between the pole faces of the magnet so that the magnetic field at the probe was equal to the magnetic field at the paramagnetic sample in the microwave cavity. This was checked by observing the paramagnetic resonance of the free radical 1-1 diphenyl -2- picryl hydrazl whose g value is known to a high degree of accuracy. By measuring the magnetic field at which resonance occurred for this free radical and the klystron frequency, the g value was measured and compared to the known value. The position of the magnetometer probe was adjusted until the free radical g value measured in the experiments coincided with the known g value to about 1 part in 4000. This insured that the accuracy of the magnetic field measurements was ± 1 gauss.

Measurement of the width of the proton resonance line observed by using the magnetometer gave an estimate of the homogeneity of the magnetic field near the sample. From such a measurement, the magnetic field was found to be homogeneous to ± 0.25 gauss over an area of 4 cm². For the samples studied in the paramagnetic resonance experiments the inhomogeneity of the magnetic field over the sample volume was small compared with the width of the lines in the resonance spectrum.

In the experiments to be described two definitions of line width are used. With the exception of Chapter III, all statements of the line width of an absorption line re-
fer to the separation, in gauss, between points of maximum and minimum slope of the line. In Chapter III, the line width is defined to be the width of an absorption line, in gauss, at half the maximum height of the line.
CHAPTER III

PARAMAGNETIC RESONANCE PROPERTIES OF Cr^{+++}
IN RUBY AT 300°K

Crystal Structure

Corundum (α - Al₂O₃) crystals which contain small amounts of Cr₂O₃ are usually referred to as ruby crystals. The presence of the Cr^{+++} ion in the corundum lattice gives the crystal a red color. The crystal structures of α - Al₂O₃ and Cr₂O₃ are isomorphous; hence, ruby can be considered basically an α - Al₂O₃ crystal in which some of the Al atoms have been replaced by Cr atoms.

The basic structure of corundum is rhombohedral and the unit cell has dimensions a₀ = 5.13 Å and α = 55°6'. A basal projection of the α - Al₂O₃ structure is shown in Fig. 8. In Fig. 9 the corundum lattice is shown in perspective. The immediate surroundings of an Al atom consist of an octahedron of oxygen atoms in which the Al atom is displaced from the center of the octahedron along its trigonal axis, which is also the three-fold axis of the unit cell. The over-all symmetry of an Al site is trigonal; consequently, the internal crystalline electric field at an Al^{+++} or Cr^{+++} ion in ruby must have trigonal symmetry about the trigonal axis of the crystal.
A basal projection of a portion of the $\alpha - \text{Al}_2\text{O}_3$ lattice on a plane normal to the three-fold axis and passing through the apex of the unit rhombohedron is shown. The small circles are the aluminum ions. The fractions give distances below the projection plane measured in terms of the height of the unit rhombohedron. The projections of the axes of the unit rhombohedron are indicated by heavy lines and the intermediate lines give the outline of its three upper faces.
Figure 9

A perspective drawing of the corundum lattice is shown. Large circles represent oxygen atoms and the small dark circles represent aluminum atoms.
Spin Hamiltonian for Cr\textsuperscript{+++} in Ruby

The effect of a trigonal crystalline electric field on the 4\textsuperscript{F} state of the Cr\textsuperscript{+++} ion is to split this state into two twofold orbitally degenerate states and three onefold orbital states all of which are \((2S + 1)\)-fold degenerate with respect to the spin. From theoretical considerations alone it cannot be decided whether an orbital singlet is the lowest energy state; however, to interpret correctly the paramagnetic resonance data for Cr\textsuperscript{+++} in ruby it is necessary to assume that an orbital singlet level is indeed lowest. As shown in Chapter I, if an orbital singlet is lowest, the influence of the spin-orbit coupling \(\lambda (L S)\) is to partially remove the spin degeneracy; this gives for Cr\textsuperscript{+++} \((S = 3/2)\) two twofold degenerate spin levels in zero magnetic field. No hyperfine structure effects need be considered because the abundant isotope Cr\textsuperscript{52} has no nuclear spin. Hence for the case of a Cr\textsuperscript{+++} ion in ruby, the spin Hamiltonian has the form

\[
\mathcal{H}_S = DS_z^2 + \beta [g_u S_z H_z + g_\perp (S_x H_x + S_y H_y)], \tag{3.1}
\]

where \(S = 3/2\) and the \(z\)-axis has been chosen to coincide with the trigonal axis of the crystal. Equation (3.1) can be written in the convenient form

\[
\mathcal{H}_S = DS_z^2 + \beta H [g_u S_z \cos \theta + g_\perp \sin \theta \{\gamma e^{i\theta} S_+ + \gamma e^{-i\theta} S_-\}], \tag{3.2}
\]
where $\theta$ is the polar angle between the z-axis of the crystal and the external magnetic field and $\phi$ is the azimuthal angle about the z axis.

In the calculation of the eigenvalues of the Hamiltonian in (3.2), it is convenient to use a representation in which the matrix elements of the operators $S^2$ and $S_z$ are diagonal. For such a representation the Hamiltonian matrix is given by

$$
(M_3, | \mathcal{H}_S | M_3) =
$$

<table>
<thead>
<tr>
<th>$M_3$</th>
<th>$1/2$</th>
<th>$-1/2$</th>
<th>$-3/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1/2$</td>
<td>$\frac{3}{2} g_| \beta H \cos \theta$ + $\frac{1}{4} D$</td>
<td>$\frac{\sqrt{3}}{2} g_| \beta H \sin \theta e^{i\phi}$</td>
<td></td>
</tr>
<tr>
<td>$-1/2$</td>
<td>$\frac{\sqrt{3}}{2} g_| \beta H \sin \theta e^{i\phi}$</td>
<td>$\frac{1}{2} g_| \beta H \cos \theta$ + $\frac{1}{4} D$</td>
<td></td>
</tr>
<tr>
<td>$-3/2$</td>
<td></td>
<td>$\frac{1}{2} g_| \beta H \cos \theta$ + $\frac{1}{4} D$</td>
<td></td>
</tr>
</tbody>
</table>

To find the energy eigenvalues it is necessary to diagonalize (3.3); however, this is difficult in general since it involves finding the roots of a general quartic equation. In the solution of the secular determinant of
(3.3) the resulting quartic equation is independent of $\phi$; hence, the paramagnetic resonance spectrum is constant as $H$ is varied in the $xy$ plane. To determine the parameters $g_{\|}, g_{\perp}$ and $D$, it is only necessary to make measurements for $\phi = 0^\circ$ and $\phi = 90^\circ$. For each of these orientations of the magnetic field with respect to the crystal, closed expressions for the energy levels can be given.

The energy expressions for $\phi = 0^\circ$ are given by

\[
\begin{align*}
E_{3/2} &= \frac{3}{2} g_{\|} \beta H + \frac{9}{2} D \\
E_{1/2} &= \frac{1}{2} g_{\|} \beta H + \frac{1}{4} D \\
E_{-1/2} &= -\frac{1}{2} g_{\|} \beta H + \frac{1}{4} D \\
E_{-3/2} &= -\frac{3}{2} g_{\|} \beta H + \frac{9}{4} D
\end{align*}
\]

Since for $\phi = 0^\circ$ equation (3.3) is a diagonal matrix, the energy levels can be identified with the magnetic quantum number $M_s$ of the operator $S_z$. For this orientation the selection rules for magnetic dipole transitions are

$\Delta M_s = \pm 1$.

When the magnetic field is perpendicular to the three-fold axis of the crystal, the matrix given by (3.3) is not diagonal; however, the secular determinant of this matrix for $\phi = 90^\circ$ can be factored into two $2 \times 2$ determinants by rearrangement of rows and columns such that the energy eigenvalues are the roots of two quadratic equations. Because (3.3) has non-zero off-diagonal elements
for θ = 90°, the energy levels cannot be identified with a single magnetic quantum number $M_s$. For this orientation the energy levels are given by

$$E_1 = D \left[ \frac{5}{4} - x - \sqrt{(1+x)^2 + 3x^2} \right]$$

$$E_2 = D \left[ \frac{5}{4} + x - \sqrt{(1-x)^2 + 3x^2} \right]$$

$$E_3 = D \left[ \frac{5}{4} - x + \sqrt{(1+x)^2 + 3x^2} \right]$$

$$E_4 = D \left[ \frac{5}{4} + x + \sqrt{(1-x)^2 + 3x^2} \right]$$

where $x = \left( \frac{g_\perp \beta H}{2D} \right)$. Magnetic-dipole transitions between all the levels in (3.5) are allowed for the case when the magnetic energy $g_\perp \beta H$ is comparable to the zero field energy $2D$. This situation is realized for Cr$^{+++}$ in ruby.

**Experimental Results**

Initial experiments$^{22}$ on the Cr$^{+++}$ paramagnetic resonance spectrum in ruby at 300°K were carried out on both a synthetic and a natural ruby crystal. The data from these measurements was best fitted to the Hamiltonian in (3.1) by setting

$$|D| = 0.193 \pm 0.001 \text{ cm}^{-1}$$

$$g_\parallel = 2.003 \pm 0.006$$

$$g_\perp = 2.00 \pm 0.02$$
The variation of the fine-structure lines with polar angle $\theta$ obtained in these measurements is shown in Fig. 10. The agreement between experimental and calculated values of the resonance fields was found to be within the experimental error for $\theta = 0^\circ$; however, for $\theta = 90^\circ$ the agreement was only good to $\pm 1$ per cent of the measured values. To check the agreement at intermediate angles, numerical tables compiled by Parker$^{23}$ were used with the assumption

$$g_{\perp} = g_{\|}.$$  

For all angles the measured values agreed with calculated line positions to within $\pm 1$ per cent of the measured values.

In these measurements the method of observing the resonance lines was different from that described in Chapter II. The absorption of microwave radiation by the sample was detected as a change in the d.c. voltage across the crystal diode detector following the cavity. This d.c. voltage was amplified and applied to the vertical plates of an oscilloscope. A small voltage proportional to the current through the magnet coils was applied to the horizontal plates of the oscilloscope, so that as the magnetic field was varied through a resonance a plot of absorbed power versus magnet current was made. A typical resonance line as observed by these methods in the natural ruby is shown in Fig. 11.

---

Figure 10

A plot of the resonance fields at 9309 Me./sec. of the Cr^{+++} fine-structure spectrum as a function of the polar angle $\Theta$ is shown.
Resonance Fields vs $\Theta$

- ○ Experimental Points
- ▲ Calculated Points

- $(E_{3/2} - E_{1/2})$
- $(E_{1/2} - E_{-1/2})$
- $(E_{1/2} - E_{3/2})$
More precise measurements on the Cr\textsuperscript{+++} paramagnetic resonance spectrum in ruby have been recently carried out with the apparatus described in Chapter II. These measurements were carried out on a natural ruby. The actual concentration of Cr in the crystal was not known; however, the light pink color of the crystal and the fact that the lines in the spectrum were only 25 gauss wide indicated that the concentration of Cr was very small. For the purpose of obtaining $g_{\parallel}$, $g_{\perp}$ and $D$, the spectrum of this crystal was studied for $\theta = 0^\circ$ and $\phi = 90^\circ$. The spectrum observed at $\nu = 8889.3$ Mc./sec. and $\theta = 0^\circ$ consisted of three lines. The fields at which these lines occurred and their relative intensities are given below.

<table>
<thead>
<tr>
<th>Approx. Rel. Intensity</th>
<th>Experimental Resonance Field (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>934.1 ± 1.0</td>
</tr>
<tr>
<td>4</td>
<td>3201.4 ± 1.0</td>
</tr>
<tr>
<td>3</td>
<td>7336.4 ± 1.0</td>
</tr>
</tbody>
</table>

The relative intensities were measured by comparing the heights of the absorption lines in the spectrum and are only a rough estimate of the actual intensity of each line. To measure the actual relative intensity of each line it is necessary to compare the area under each absorption line. This was not done in the experiments.
Figure 11

An oscilloscope trace of one of the fine structure lines observed in a single natural ruby crystal is shown. The width of the line shown was 45 gauss.
theoretical relative intensities which are given later compare the power absorbed by the sample for the various transitions.

For $\theta = 90^\circ$ and $\nu = 8887.0$ Mc./sec. the spectrum consisted of two lines. The fields at which these two lines occur and their relative intensities are given below.

<table>
<thead>
<tr>
<th>Approx. Rel. Intensity</th>
<th>Experimental Resonance Field (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$1793.6 \pm 1.0$</td>
</tr>
<tr>
<td>1</td>
<td>$5142.5 \pm 1.0$</td>
</tr>
</tbody>
</table>

If one considers $g_\parallel$, $g_\perp$ and $D$ as independent constants, then the sign of $D$ cannot be inferred from the resonance spectra. In (1.16), however, it is seen that $g_\parallel$, $g_\perp$ and $D$ are related in the following manner

$$\lambda (g_\parallel - g_\perp) = 2D.$$ 

Since $g_\parallel$ and $g_\perp$ are positive and $\lambda$ is positive for Cr$^{+++}$, it is evident that if $g_\perp$ is greater than $g_\parallel$, then $D$ is a negative quantity. The more accurate measurements give $g_\perp$ larger than $g_\parallel$ for Cr$^{+++}$ in ruby. In view of this, the lines observed for $\theta = 0^\circ$ and $\theta = 90^\circ$ can be assigned to definite transitions.

Let us consider first the lines observed for $\theta = 0^\circ$. The line with intensity $4$ was assigned to the transition $(E_{1/2} - E_{-1/2})$ from which $g$ is found to be $1.984 \pm 0.001$. 

The line at 934.1 gauss was assigned to the transition \( (E_{1/2}^1 - E_{3/2}^1) \) and the line at 7336.4 gauss was assigned to the transition \( (E_{3/2}^1 - E_{1/2}^1) \). From these transitions it is found that \( 2D = -0.3831 \pm 0.0002 \text{ cm}^{-1} \). If these values of \( g_\parallel \) and \( 2D \) are used, the position of the lines predicted by theory and their theoretical relative intensity are listed below.

<table>
<thead>
<tr>
<th>Theo. Resonance Field (gauss)</th>
<th>Theo. Rel. Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>934.7</td>
<td>3</td>
</tr>
<tr>
<td>3201.4</td>
<td>4</td>
</tr>
<tr>
<td>7336.9</td>
<td>3</td>
</tr>
</tbody>
</table>

For \( \theta = 90^\circ \) the line at 1793.6 gauss was assigned to the transition \( (E_2^1 - E_1^1) \) and the one at 5142.5 gauss was assigned to the transition \( (E_4^1 - E_3^1) \). With this assignment and with the value of \( D \) obtained from \( \theta = 0^\circ \) measurements, \( g_\perp \) can be calculated and is found to be \( 1.987 \pm 0.002 \). With this value of \( g_\perp \) and \( D \) as obtained before, the position of the lines predicted by theory are listed below.

<table>
<thead>
<tr>
<th>Theo. Resonance Fields (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1794.3</td>
</tr>
<tr>
<td>5141.9</td>
</tr>
</tbody>
</table>
No attempt was made to calculate the theoretical relative intensities for the lines observed when $\Theta = 90^\circ$.

Conclusions

The results of the more recent measurements, because of their internal consistency, establish that the spin Hamiltonian in (3.1) with

$$g_{II} = 1.984 \pm 0.001$$

$$g_\perp = 1.987 \pm 0.002$$

$$2D = -0.3831 \pm 0.0002 \text{ cm}^{-1}$$

describes the magnetic resonance properties of Cr$^{+++}$ in ruby. The discrepancies in the earlier measurements are assigned to some systematic misalignment of the crystal for $\Theta = 0^\circ$. It is seen from Fig. 10 that a misalignment of about $1^\circ$ for this position causes an error in $g_{II}$ of approximately 1 per cent. The error is of such a nature that the apparent $g_{II}$ will be larger than the actual value.

The results of the experiments are in substantial agreement with measurements made by other workers. M. Zaripov and I. Shamonin$^{24}$ have obtained the values


$$g_{II} = g_\perp = 1.98$$

$$|2D| = 0.38 \text{ cm}^{-1}$$
whereas Manenkov and Prokhorov\textsuperscript{25} give the values

\begin{align*}
g_u &= 1.984 \pm 0.0006 \\
g \downarrow &= 1.9867 \pm 0.0006 \\
|2D| &= 0.3824 \text{ cm}^{-1}.\end{align*}

The slight disagreement between the latter value of $2D$ and the value obtained in the present measurements cannot be resolved at present in view of the vague statements of accuracy given in the Russian articles.
CHAPTER IV

PARAMAGNETIC RESONANCE PROPERTIES OF Fe+++ IN BLUE SAPPHIRE AT 300°K

Crystals of $\alpha$-Al$_2$O$_3$ which contain small amounts of Fe$_2$O$_3$ are referred to as blue sapphires. Because of the similarity of structure, the Fe atoms substitute for the Al atoms in the $\alpha$-Al$_2$O$_3$ lattice. The Fe$^{+++}$ ion in blue sapphire like the Cr$^{+++}$ ion in ruby is subjected to a crystalline electric field of trigonal symmetry.

**Spin Hamiltonian for Fe$^{+++}$ in Blue Sapphire**

The ground state of the Fe$^{+++}$ ion is $^6S$. If one applies the arguments which have been presented in Chapter I to the case of an S state ion ($L = 0$), one finds that the crystal field can cause no splitting of the spin levels since there is no orbital degeneracy and the term $\lambda (L \cdot S)$ is zero. However it is well known that splittings of the spin levels in zero magnetic field due to the crystalline electric fields actually exist for S state ions in the iron group.

Van Vleck and Penney have explained the splitting

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by assuming that there exists a small amount of j-j coupling
which distorts the spherically symmetric charge distribution of an $S$ state. Abragam and Pryce\textsuperscript{11} have come to the conclusion that the splittings observed experimentally are too large to be explained by the process proposed by Van Vleck and Penney. They suggest instead that the splittings are due to a spin-spin interaction of the form

$$\sum_{j,\kappa} 4\beta^2 \left[ \frac{\mathbf{s}_j \cdot \mathbf{s}_\kappa}{r_{jk}^3} - 3 \frac{(\mathbf{r}_j \cdot \mathbf{s}_j)(\mathbf{r}_\kappa \cdot \mathbf{s}_\kappa)}{r_{jk}^5} \right]$$

which couples orbits with spins, since it depends on the position coordinates of the electrons. They argue that in the crystal field, even though the ion is in an $S$ state, there will be some distortion of the orbital motion of the electrons. Because of this distortion by the crystal field the electron cloud is non-spherical. The dipole-dipole energy of the individual electrons given in (4.1) varies with orientation of $\mathbf{r}$ with respect to the crystal field and thus the eigenvalues of energy depend on the orientation of the spins with respect to the crystal. With this type of argument Abragam and Pryce calculate magnitudes of the splittings which agree with experimentally observed splittings of the spin levels in zero magnetic field.

The resonance spectrum of the ferric ion in sapphire can be analyzed in terms of a spin Hamiltonian which
reflects the symmetry of the crystalline electric field. One form in which the spin Hamiltonian for the case of trigonal symmetry can be written is given by

\[ H_s = g_\beta \mathbf{H} \cdot \mathbf{S} + D \left\{ 3S^2 - s(s+1) \right\} \\
+ F \left\{ 35S^4 - 30S(s+1)S^2 + 25S^2 - 6S(s+1) + 3s^2(s+1)^2 \right\} \\
+ \frac{g}{\sqrt{2}} \left\{ \left[ S_z (s_+^3 + s_-^3) + (s_+^3 + s_-^3) S_z \right] \\
+ i \left[ S_z (s_+^3 - s_-^3) + (s_+^3 - s_-^3) S_z \right] \right\} \quad (4.2) \]

In (4.2) the z-axis has been chosen to coincide with the three-fold axis of the crystal. In a representation in which \( S_z \) and \( S^2 \) are diagonal the Hamiltonian matrix of (4.2) is given by

\[
\begin{array}{cccccc}
\text{M} & \text{H} & \text{M} \\
\hline
5/2 & 3/2 & 1/2 & -1/2 & -3/2 & -5/2 \\
5/2 & 1/2 & 3/2 & 1/2 & -1/2 & -5/2 \\
3/2 & 1/2 & 3/2 & 1/2 & -1/2 & -5/2 \\
1/2 & 3/2 & 1/2 & 5/2 & -3/2 & \sqrt{2}G(1-i) \\
-1/2 & 3/2 & 1/2 & 5/2 & -3/2 & \sqrt{2}G(i+1) \\
-3/2 & 1/2 & 3/2 & 1/2 & -1/2 & -5/2 \\
-5/2 & 1/2 & 3/2 & 1/2 & -1/2 & -5/2 \\
\end{array}
\]
For some arbitrary direction of $H$ relative to the $z$-axis, the energy eigenvalues are solutions of a general sixth-degree equation. Only if $H$ is parallel to the $z$-axis can the energy eigenvalues be given in closed form. In this case, the Hamiltonian matrix (4.3) can be put into the following form

$$ (M_z | M_z ) = $$

<table>
<thead>
<tr>
<th>$\frac{5}{2}$</th>
<th>$-\frac{1}{2}$</th>
<th>$\frac{1}{2}$</th>
<th>$-\frac{5}{2}$</th>
<th>$\frac{3}{2}$</th>
<th>$-\frac{3}{2}$</th>
</tr>
</thead>
</table>
| $\begin{array}{c}
10D+60F \\
\frac{1}{2} + \frac{3}{2} g\beta H
\end{array}$ | $\begin{array}{c}
2i5G(i+i) \\
-8D+120F \\
-\frac{1}{2} g\beta H
\end{array}$ | $\begin{array}{c}
\frac{1}{2} + 2i5G(-i) \\
-8D+120F \\
-\frac{1}{2} g\beta H
\end{array}$ | $\begin{array}{c}
10D+60F \\
\frac{1}{2} + \frac{3}{2} g\beta H
\end{array}$ | $\begin{array}{c}
\frac{1}{2} + 2i5G(i+i) \\
-8D+120F \\
-\frac{1}{2} g\beta H
\end{array}$ | $\begin{array}{c}
-2D-180F \\
-\frac{3}{2} g\beta H
\end{array}$ |

It is evident from (4.4) that four of the energy eigenvalues for $H$ parallel to the $z$ direction are given as the roots of two quadratic equations and the remaining two energy eigenvalues are given by the matrix elements $(\frac{3}{2}, | M_\sigma = \frac{3}{2} )$ and $( -\frac{3}{2}, | M_\sigma = -\frac{3}{2} )$ of (4.4). For the analysis of the spectrum for $H$ parallel to the three-
fold axis, the exact energy expressions give rise to complicated expressions for the transitions; hence, a perturbation treatment is carried out instead so that the constants $g$, $D$, $F$ and $G$ can be evaluated from the data. In the perturbation treatment for $H$ parallel to the $z$-axis, the zero-order Hamiltonian is taken to be

$$\mathcal{H}^0_z = g \beta HS_z + D \left\{ 3S_z^2 - S(S+1) \right\} + F \left\{ 35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2 \right\}$$

and the perturbing Hamiltonian is given by

$$\mathcal{H}'_z = \frac{g}{\sqrt{2}} \left\{ [S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3) S_z] + 1 [S_z(S_+^3 - S_-^3) + (S_+^3 - S_-^3) S_z] \right\}.$$ 

The energy levels to second order for this case are given by

$$E_{5/2} = \left\{ 10D + \frac{5}{2}g\beta H + 60F \right\} + \frac{1440G^2}{(18D - 60F) + 3g\beta H}$$

$$E_{3/2} = \left\{ -2D + \frac{3}{2}g\beta H - 180F \right\}$$

$$E_{1/2} = \left\{ -8D + \frac{1}{2}g\beta H + 120F \right\} + \frac{1440G^2}{(-18D + 60F) + 3g\beta H}$$

$$E_{-1/2} = \left\{ -8D - \frac{1}{2}g\beta H + 120F \right\} + \frac{1440G^2}{(-18D + 60F) - 3g\beta H}$$

$$E_{-3/2} = \left\{ -2D - \frac{3}{2}g\beta H - 180F \right\}$$

$$E_{-5/2} = \left\{ 10D - \frac{5}{2}g\beta H + 60F \right\} + \frac{1440G^2}{(18D - 60F) - 3g\beta H}$$
where the levels are identified with the zero-order energies. Since \( g \) is isotropic, all the constants can be evaluated from resonance data for \( H \) parallel to the \( z \)-axis.

A perturbation treatment cannot be carried out for \( H \) perpendicular to the three-fold axis because for \( \text{Fe}^{3+} \) in sapphire the zero-field splittings are of the order of magnitude of the magnetic splittings.

**Experimental Results**

A synthetic blue sapphire crystal containing approximately 0.02% of \( \text{Fe}^{2+} \) was used in the experiments. The sample studied was cut from a half inch sphere which was obtained from Professor J. G. Daunt. The external shape of the sample studied was a rectangular solid with the three-fold axis perpendicular to one of the faces to within \( \pm 1/2^\circ \) as determined by optical measurements.

The widths of the resonance lines observed in this crystal were approximately 10 to 15 gauss. To obtain the parameters \( g, D, F \) and \( G \) in the spin Hamiltonian \((4.2)\), the paramagnetic resonance spectrum was measured for the case when the trigonal axis of the crystal was parallel to the magnetic field. The spectrum observed in this orientation at \( \nu = 5553.0 \text{ Mc./sec.} \) consisted of four lines. The fields at which these lines occurred and their estimated relative intensities are given in the following.
The relative intensities were measured by comparing the heights of the absorption lines in the spectrum. This method of estimating the relative intensities is subject to error if the lines in the spectrum are of different widths. To measure the intensity of each line accurately it is necessary to measure the area under each absorption line. Since this was not done in the experiments the relative intensities given above can only be considered as a rough indication of the strength of each line and should not be taken too seriously.

A tentative set of assignments of the observed lines were made. The line at 3272 gauss was assigned to the \((E_{1/2} - E_{-1/2})\) transition, the line at 1025 gauss to the \((E_{-3/2} - E_{-1/2})\) transition and the line at 7365 gauss to the transitions \((E_{-1/2} - E_{-3/2})\) and \((E_{-5/2} - E_{-3/2})\).

This double assignment for the line at 7365 gauss is justified, for when the trigonal axis of the crystal makes an angle of 10° with the magnetic field, two lines are
observed near 7365 gauss. These lines which have been assigned correspond to $\Delta M_s = \pm 1$ transitions in zero-order notation. The line at 3767 gauss is assigned to the "double jump" transition \( (E_{1/2} - D_{-3/2}) \). On the basis of these assignments and the perturbation expressions for the energy levels given in (4.7) the constants which appear in the spin Hamiltonian are found to be

\begin{align*}
g &= 2.003 \pm 0.008 \\
D &= 7.67 \pm 0.02 \times 10^{-2} \text{ cm}^{-1} \\
F &= 2.31 \pm 0.03 \times 10^{-4} \text{ cm}^{-1} \\
|G| &= 1.93 \pm 0.4 \times 10^{-3} \text{ cm}^{-1}.
\end{align*}

From the resonance spectrum alone, the sign of $D$ cannot be determined, but if $D$ is assumed positive then $F$ is found also to be positive. The estimated error which is quoted is based on a consideration of the relative size of the contributions of the constants in determining the magnetic-field positions of the lines observed in the spectrum. With these values of $g$, $D$, $F$ and $G$, the positions of lines with non-zero intensities predicted by second-order perturbation theory are given below.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( (E_{-3/2} - E_{1/2}) )</td>
<td>0.02</td>
<td>520</td>
<td>Not obs.</td>
</tr>
<tr>
<td>( (E_{-3/2} - E_{-1/2}) )</td>
<td>8.0</td>
<td>1034</td>
<td>+9</td>
</tr>
<tr>
<td>( (E_{-5/2} - E_{3/2}) )</td>
<td>0.06</td>
<td>1817</td>
<td>Not obs.</td>
</tr>
<tr>
<td>( (E_{1/2} - E_{3/2}) )</td>
<td>8.8</td>
<td>3273</td>
<td>+1</td>
</tr>
<tr>
<td>( (E_{1/2} - E_{-1/2}) )</td>
<td>0.3</td>
<td>3761</td>
<td>-6</td>
</tr>
<tr>
<td>( (E_{3/2} - E_{-5/2}) )</td>
<td>0.2</td>
<td>3442</td>
<td>Not obs.</td>
</tr>
<tr>
<td>( (E_{-5/2} - E_{-1/2}) )</td>
<td>0.5</td>
<td>5572</td>
<td>Not obs.</td>
</tr>
<tr>
<td>( (E_{-5/2} - E_{-3/2}) )</td>
<td>5.0</td>
<td>7352</td>
<td>-13</td>
</tr>
<tr>
<td>( (E_{-1/2} - E_{-3/2}) )</td>
<td>8.0</td>
<td>7354</td>
<td>-11</td>
</tr>
</tbody>
</table>

The theoretical intensities were calculated by using wave functions which are valid to first order in perturbation theory. The column labeled \( Δ \) gives the theoretical position minus the observed line position. It is to be noted that theory predicts the \( (E_{-1/2} - E_{-3/2}) \) and \( (E_{-5/2} - E_{-3/2}) \) transitions to be separated by 2 gauss. Since the widths of the lines observed in the spectrum were approximately 10 gauss, these two lines would not be resolved. The theory predicts four lines which were not observed for \( H \parallel \) trigonal axis. The \( (E_{-3/2} - E_{1/2}) \) transition predicted at 520 gauss is very weak and it is understandable that this line is not observed. If the crystal is rotated away from \( H \) being parallel to the trigonal axis, a weak line appears at approximately 517 gauss which is probably the \( (E_{-3/2} - E_{1/2}) \).
transition. It is not understood why the other transitions 
(E_{-5/2} - E_{3/2}), (E_{3/2} - E_{-5/2}) and (E_{-5/2} - E_{-1/2}) are not 
observed. For the latter two transitions the expected 
theoretical intensities are approximately equal to the in-
tensity of the transition (E_{1/2} - E_{-3/2}) which was observed.

One possible explanation for these lines not being 
obscured is that these transitions are broadened by crystal 
imperfections more than the observed "double jump" transi-
tion, since they are more dependent on the constants D and 
F in the spin Hamiltonian. If this explanation were cor-
rect, the absorption lines between levels involving 
M_s = \pm 3/2, \pm 5/2 would be broader than the transition 
(E_{1/2} - E_{-1/2}). However, the observed lines were all of 
the same width (10-15 gauss). The reason for the absence 
of the transitions (E_{3/2} - E_{-5/2}) and (E_{-5/2} - E_{1/2}) re-
mains obscure.

The agreement between line positions calculated 
from second order perturbation theory and those observed 
experimentally indicates that the tentative assignments 
given for the lines observed in the spectrum for H//trig-
ronal axis is probably correct. Better agreement would 
probably be obtained if the exact expressions for the energy 
levels had been used. The present experiments indicate 
that a similar experiment at a much higher microwave fre-
quency is necessary to verify the correctness of the 
assignments which have been made.
The paramagnetic resonance spectrum was also observed for $H$ perpendicular to the trigonal axis of the crystal. For this orientation only two lines are observed at $\nu = 8885.7$ Mc./sec.. The position of these lines and their relative intensities are given below.

**H $\perp$ Trigonal Axis ($\nu = 8885.7$ Mc./sec.)**

<table>
<thead>
<tr>
<th>Approx. Rel. Int.</th>
<th>Experimental Resonance Field (gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1218 \pm 1$</td>
</tr>
<tr>
<td>1</td>
<td>$3202 \pm 1$</td>
</tr>
</tbody>
</table>

For this orientation no analysis of the spectrum has been made, because of the complicated nature of the energy level expressions for this orientation.

A typical absorption line which was observed for Fe$^{+++}$ in sapphire is shown in Fig. 12.
A typical absorption line observed for Fe$^{+++}$ in sapphire is shown. The $(E_{-3/2} - E_{-1/2})$ transition is shown for $H$ parallel to the trigonal axis.

The klystron frequency was 3883 Mc./sec.
Klystron Freq. 8883 Mc/sec.

\[(E_{-\frac{3}{2}} - E_{-\frac{1}{2}})\] Transition of Fe\(^{+++}\)

In Sapphire For H II Trigonal Axis
COMPUTATION OF THE PRINCIPAL COMPONENTS OF AN ASYMMETRIC (g) TENSOR FROM PARAMAGNETIC RESONANCE DATA

For the case of a paramagnetic ion having no nuclear spin and having \( S = 1/2 \), the paramagnetic resonance properties of the ion in a crystal can be predicted from a spin Hamiltonian of the form

\[
\mathcal{H}_s = \beta \mathbf{H} \cdot (g) \cdot \mathbf{S} = \sum \beta g_{ij} H_i S_j
\]  

(5.1)

where \( \mathbf{H} \) and \( \mathbf{S} \) are vectors and \( (g) \) is a symmetric second order tensor. In the principal coordinate system of the \( (g) \) tensor the Hamiltonian takes the simpler form given by

\[
\mathcal{H}_s = \beta \left[ g_x' H_x S_x + g_y' H_y S_y + g_z' H_z S_z \right].
\]  

(5.2)

To describe completely the paramagnetic resonance properties of the ion, the constants \( g_x', g_y' \) and \( g_z' \) must be evaluated from experimental data. Also the orientation of the principal coordinate system relative to the crystal axes has to be determined.

When the direction of the principal coordinates relative to the crystal axes can be inferred from the symmetry properties of the crystal, the determination of the constants \( g_x', g_y' \) and \( g_z' \) is indeed simple. However, in
many cases, the orientation of the principal coordinate system is not suggested by the symmetry properties of the crystal. For the latter situation a method will be outlined by which one can obtain in a simple and direct manner the components \((g^2)_{ij}\) of the \((g^2)\) tensor from rotation data about any three mutually orthogonal reference axes whose relations to the crystal axes are known. Finally from the components of the \((g^2)\) tensor the principal \(g\) components and the orientation of the principal coordinate system of the \((g)\) tensor relative to the reference orthogonal system are found.

To describe the method\(^{27}\) it is first necessary to choose some convenient orthogonal \(xyz\) coordinate system which is fixed relative to the crystal. In such a coordinate system the spin Hamiltonian has the form

\[
\mathcal{H}_s = \beta \left[ g_{xx} H S + g_{yy} H S + g_{zz} H S + \right. \\
+ g_{xy} (H S + H S) \\
+ g_{xz} (H S + H S) \\
+ g_{yz} (H S + H S) \left. \right] .
\]

\((5.3)\)

Consider first a rotation of the crystal about the \(z\)-axis such that the magnetic field \(H\) is in the \(xy\) plane. For
rotations of the crystal about the z-axis the spin Hamiltonian (5.3) reduces to

\[ H_s = \beta \left[ g_{xx} H_x S_x + g_{yy} H_y S_y + g_{xy} (H_x S_y + H_y S_x) \right. \]
\[ \left. + g_{xz} H_z S_z + g_{yz} H_z S_z \right] \]

If a representation in which the operators \( S_z \) and \( S^2 \) are diagonal is chosen, then the Hamiltonian matrix is given by

\[ (M_\phi | H_s | M_\phi) = \frac{1}{2} \beta \left[ \begin{array}{cc} a & b - ic \\ b + ic & -a \end{array} \right] \] (5.5)

where we have assumed

\[ H_x = H \cos \phi \]
\[ H_y = H \sin \phi \]
\[ H_z = 0 \]

and

\[ a = (g_{yz} \sin \phi + g_{xz} \cos \phi) \]
\[ b = (g_{xy} \sin \phi + g_{xx} \cos \phi) \]
\[ c = (g_{yy} \sin \phi + g_{xy} \cos \phi) \]

The eigenvalues of the energy can be found by diagonalizing (5.5) and are found to be

\[ E = \pm \frac{1}{2} \beta H \sqrt{a^2 + b^2 + c^2} \] (5.6)
The transition between these two levels is given by

\[ \hbar \nu = \beta H \sqrt{a^2 + b^2 + c^2} \]

and

\[ g^2 = \left( \frac{\hbar \nu}{\beta H} \right)^2 = a^2 + b^2 + c^2 \]  \hspace{1cm} (5.7)

\[ = C_{11} \cos^2 \varphi_z + C_{22} \sin^2 \varphi_z + 2C_{12} \sin \varphi_z \cos \varphi_z. \]

The constants $C_{11}$, $C_{22}$, and $C_{12}$ can be determined from the experimental data and are related to the $g_{ij}$'s in the following manner:

\[ C_{11} = g_{xx}^2 + c_{xy}^2 + c_{xz}^2 \]

\[ C_{22} = c_{xy}^2 + g_{yy}^2 + c_{yz}^2 \]  \hspace{1cm} (5.8)

\[ 2C_{12} = 2C_{21} = 2(g_{yz} g_{xz} + g_{xy} g_{xx} + g_{yy} g_{xy}). \]

In the same manner one can consider the rotation of the crystal about the $x$-axis and obtain the relations

\[ g^2 = \left( \frac{\hbar \nu}{\beta H} \right)^2 = C_{22} \cos^2 \varphi_x + C_{33} \sin^2 \varphi_x + 2C_{23} \sin \varphi_x \cos \varphi_x \]  \hspace{1cm} (5.9)

where again $C_{22}$, $C_{33}$, and $C_{23}$ are experimentally determined constants. For this case $\varphi_x$ is defined as follows

\[ H = H \cos \varphi \]

\[ y = H \sin \varphi \]

\[ H = 0 \]
Finally for rotations about the y-axis we obtain

\[ g^2 = \left( \frac{h \nu}{\beta H} \right)^2 = c_{33} \cos^2 \phi + c_{11} \sin^2 \phi + 2c_{13} \sin \phi \cos \phi \] (5.11)

where

\[ H_x = H \cos \phi \]
\[ H_y = H \sin \phi \]
\[ H_z = 0 \]

and

\[ c_{33} = g_{zz}^2 + g_{xz}^2 + g_{yz}^2 \]
\[ c_{11} = g_{xx}^2 + g_{xy}^2 \] (5.12)
\[ 2c_{31} = 2c_{13} = 2(g_{xz}g_{xx} + g_{xy}g_{xx} + g_{yz}g_{xy}) \]

From (5.8), (5.10) and (5.12) one obtains six linearly independent equations relating the experimentally determined constants to the \( g_{ij} \)'s.
The direct solution of the \( g_{ij} \)'s from these equations is by no means simple. However to determine the principal \( g \) values this is not necessary. To show how the principal \( g \)'s are determined, the set of equations given in (5.13) are written below in matrix form.

\[
\begin{pmatrix}
g_{xx} & g_{xy} & g_{xz} \\
g_{xy} & g_{yy} & g_{yz} \\
g_{xz} & g_{yz} & g_{zz}
\end{pmatrix}^2 =
\begin{pmatrix}
c_{11} & c_{12} & c_{13} \\
c_{21} & c_{22} & c_{23} \\
c_{31} & c_{32} & c_{33}
\end{pmatrix}
\]

(5.14)

To find the principal \( g \) values it is necessary to find a transformation \( (\alpha) \) such that

\[
(\alpha) (g) (\alpha)^T = (g')
\]

(5.15)

where the \( (g') \) matrix is diagonal, with the diagonal
elements equal to the principal g values. From (5.15) it is obvious that

\[ (\alpha) (g^2) (\alpha) = (g')^2. \]  

(5.16)

Hence to find the principal g values it becomes necessary to diagonalize the matrix of the experimentally determined constants given in (5.14). The square of the principal g values are therefore found by solving the secular determinant given by

\[
\begin{vmatrix}
C_{11} - \lambda & C_{12} & C_{13} \\
C_{21} & C_{22} - \lambda & C_{23} \\
C_{31} & C_{32} & C_{33} - \lambda
\end{vmatrix} = 0. 
\]  

(5.17)

Once the principal g values have been obtained from (5.17), the transformation matrix (\alpha) can be found by usual mathematical methods. The matrix (\alpha) then describes the orientation of the principal coordinate system relative to the reference system.

This method, which has been outlined, was originally developed for the purpose of aiding in the interpretation of experimental data which is presented in the next chapter. However it was found that the data for topaz could not be fitted to such a simple Hamiltonian as has been discussed. A plot of g^2 vs. angle \(\phi\) for the paramagnetic center in topaz revealed that the g^2 variation contained
cos $4\theta$ and sin $4\theta$ terms which could not be neglected. These sin $4\theta$ and cos $4\theta$ terms would not be expected if the effective spin Hamiltonian for the paramagnetic center in topaz had the same form as given in (5.1). 

An alternative derivation of the expressions in (5.13) has been pointed out by Professor Jon Korringa in a private communication. The derivation given by Professor Korringa generalizes the results given in (5.13) and (5.17) to values of $S$ greater than 1/2.
CHAPTER VI

PARAMAGNETIC RESONANCE SPECTRUM OF A SINGLE TOPAZ CRYSTAL AT 300°K.

Several single crystals of topaz (Al F)₂ SiO₄ from the Thomas Mountains in Utah were found to give interesting paramagnetic resonance spectra. (OH)⁻¹ groups are known to replace fluorines in the topaz structure, but the replacement does not exceed 2.5%. The presence of such a small concentration of (OH)⁻¹ groups in the topaz lattice would be difficult to observe in the present experiments and hence only fluorines are considered. A spectrographic (optical arc spectrum) analysis indicated that small amounts of Cr and Fe were present in the crystals which were studied.

The paramagnetic resonance spectra observed could not be ascribed to either Cr or Fe ions in the lattice. However from the symmetry properties of the resonance spectra as the crystal was rotated with respect to the magnetic field and from the hyperfine structure which is present, the paramagnetic center was identified with Al sites in the crystal.
Crystal Structure

Topaz is orthorhombic\textsuperscript{28,29} with a unit cell containing four molecules. The dimensions of the unit cell are $a_o = 4.64\text{Å}$, $b_o = 8.78\text{Å}$, and $c_o = 8.37\text{Å}$. A basal projection of the topaz crystal is shown in Fig. 13. As Fig. 13 suggests, each silicon ion is surrounded by a tetrahedron of oxygen ions. Each aluminum ion is surrounded by an octahedron of anions, four of the anions are oxygens and two of the anions are fluorines. In the structure no two tetrahedra have anions in common, but each tetrahedron shares each of its oxygens with aluminum octahedra. Also each fluorine ion in the crystal is shared by two aluminum octahedra.

The surroundings of each aluminum site in the crystal are identical. However there are eight different orientations of the Al site with respect to the crystal axes. By an inversion of four of these sites, the other four sites are obtained. Hence, as far as the magnetic resonance spectra are concerned, there are only four distinguishable orientations of an Al site in the crystal. Fig. 14 shows these four distinguishable Al sites. In this figure only the immediate neighbors of each of the...
Al sites are shown. When the magnetic field is not in either the [001], [100] or [010] crystal planes, each of the four sites is differently oriented with respect to the magnetic field. If the paramagnetic center is at an Al site, it is to be expected that the spectrum would consist of four sets of lines. A given set of lines being due to one of the four distinguishable orientations of an Al site.

It is evident from Fig. 14 that any three sites can be obtained from the fourth by reflections through crystal planes followed possibly by an inversion. This can be understood in the following manner while referring to Fig. 14. The method of obtaining sites II, III and IV from site I are listed below.

To obtain II - Reflect I through [001] plane
To obtain III- Reflect I through [100] plane
To obtain IV - Reflect I through [001] plane followed by a reflection through [100] plane or reflect I through [010] plane followed by an inversion.

Consider rotations of the crystal about the a, b and c axes in turn such that the magnetic field is perpendicular to the axis of rotation. If a plane P is defined such that it contains the magnetic field H and is perpendicular to the axis of rotation, it is clear that if one site is obtained from another by reflection through the
Figure 13

A projection of topaz on the [010] plane is shown. The largest circles are oxygens, large circles marked with an F are fluorines, the smallest circles are silicons and the intermediate circles are aluminum atoms. The fractions give distances, above and below the plane of the paper, in terms of $b_0$. 
Figure 14

The four different orientations of an Al site are shown. These four aluminum octahedra are projected on the [010] plane. Large circles marked with an F are fluorines and unmarked large circles are oxygens. The small circles are the aluminum.
plane $P$ or by a reflection through $P$ followed by an inversion, then the magnetic field will make equal angles with each of these sites and their magnetic resonance spectra will be indistinguishable.

If we assume that the paramagnetic center is at Al sites, the sites which are indistinguishable or "pair off" during a given rotation are listed below.

- **a-axis rotation**
  - I and III pair off
  - II and IV pair off

- **b-axis rotation**
  - I and IV pair off
  - II and III pair off

- **c-axis rotation**
  - I and II pair off
  - III and IV pair off

This indicates that, if the paramagnetic center is at Al sites, then during rotations about the crystal axes only two sets of lines would be expected for each rotation. In addition, when the magnetic field is directed along one of the crystal axes, all four sites are indistinguishable and the two sets of lines should be coincident.

If the paramagnetic center happened to be in silicon sites, the conditions placed on the spectra by symmetry considerations would be different from the conditions which the spectra must satisfy if the paramagnetic center is at an Al site. In the next section it will be shown that the paramagnetic resonance spectra observed in topaz satisfy all the requirements for paramagnetic centers at
Al sites. In addition the hyperfine structure observed tends to substantiate this identification of the paramagnetic centers with Al sites in the crystal.

**Experimental Results**

One of the crystals of topaz from Utah was studied in detail. Its paramagnetic resonance spectrum was identical with the spectra of other crystals from this locality. The single crystal used in the measurements had well defined external features, from which the directions of the crystal axes could be inferred. The crystal was oriented on the quartz rod by optical methods with an accuracy of alignment of $\pm 1^\circ$. Better alignment of the crystal was achieved by observing the spectrum when one of the crystal axes was parallel to the magnetic field. For this position only one set of lines is observed, and the spectrum is used to check the alignment of the crystal. For each rotation about the three crystal axes, the crystal was mounted and remounted several times until satisfactory alignment of the crystal was achieved.

The paramagnetic resonance spectra of this crystal was studied for rotations of the crystal about the a, b, and c axes, such that the direction of the magnetic field relative to the crystal was varied in the [100], [010] and [001] planes respectively. For each rotation the resonance spectrum was measured at $10^\circ$ intervals. Only two sets of lines were observed when the sample was rotated.
about a crystal axis. Each set of lines exhibited a large anisotropy and each set consisted of a hyperfine triplet. The separation between hyperfine lines of a given set was $27 \pm 2$ gauss and the intensity of the hyperfine components was $1:2:1$. A typical resonance spectrum for the magnetic field in the [010] plane and making an angle of $30^\circ$ with the b-axis is shown in Fig. 15.

The variation of the two sets of lines observed for rotations about the crystal axes is shown in Figs. 16, 17 and 18. In each of these figures, only the magnetic field position of the central hyperfine component for a given set is plotted; this has been done because the hyperfine structure was found to be isotropic to within the experimental error of $\pm 2$ gauss in measuring the hyperfine structure separation. A Fourier analysis was made of each of these plots of resonance field vs. angle $\phi$ by a standard method.\textsuperscript{30} To describe the variation of the lines correctly,


the functional dependence of the resonance field $H_R$ with angle $\phi$ was found to be

$$H_R = a_0 + a_1 \cos 2\phi + b_1 \sin 2\phi + a_2 \cos 4\phi + b_2 \sin 4\phi.$$  

The Fourier coefficients were calculated for both curves in each rotation. With an estimated error of $\pm 1$ gauss for each experimental point, the error in the constant term $a_0$
The first derivative of the paramagnetic resonance spectrum in topaz is shown for the magnetic field in the [010] plane and at an angle of $30^\circ$ with the c-axis. The microwave frequency was 8951.2 Mc./sec.
A plot of resonance field vs. $\varphi_a$ for the rotation of the crystal about the a-axis relative to the magnetic field is shown. Only the central hyperfine component of each set of lines is plotted. The smooth curves are the functions

$$H_A = 1527 + 77 \cos 2\varphi_a + 159 \sin 2\varphi_a - 13 \cos 4\varphi_a + 17 \sin 4\varphi_a$$

$$H_B = 1527 + 77 \cos 2\varphi_a - 159 \sin 2\varphi_a - 13 \cos 4\varphi_a - 17 \sin 4\varphi_a$$

where the coefficients are given in gauss.

The klystron frequency was 8951.4 Mc./sec.
Figure 17

A plot of resonance field vs. $\phi_b$ for the rotation of the crystal about the b-axis relative to the magnetic field is shown. The smooth curves are the functions

\[ H_c = 1541 - 93 \cos 2\phi_b + 13^4 \sin 2\phi_b - 11 \cos 4\phi_b - 25 \sin 4\phi_b \]

\[ H_d = 1541 - 93 \cos 2\phi_b - 13^4 \sin 2\phi_b - 11 \cos 4\phi_b + 25 \sin 4\phi_b \]

where the coefficients are given in gauss.

The klystron frequency was 8951.4 Mc./sec.
A plot of resonance field vs. $\phi_c$ for the rotation of the crystal about the $c$-axis relative to the magnetic field is shown. The smooth curves are the functions

$$H_E = 1604 -16 \cos 2\phi_c + 31 \sin 2\phi_c + 2 \cos 4\phi_c - 1 \sin 4\phi_c$$

$$H_F = 1604 -16 \cos 2\phi_c -31 \sin 2\phi_c + 2 \cos 4\phi_c + 1 \sin 4\phi_c$$

where the coefficients are given in gauss.

The klystron frequency was 8951.4 Mc./sec.
was $\pm 0.3$ gauss and the error in the sine and cosine coefficients was $\pm 0.5$ gauss.

When the magnetic field direction was not in either the $[100]$, $[010]$ or $[001]$ crystal planes, the paramagnetic resonance spectrum was found to be composed of four sets of hyperfine triplets. Fig. 19 shows one of the hyperfine triplets for such an orientation of the crystal.

Conclusions

From the experimental data it is concluded that the paramagnetic centers which give rise to resonance spectra are at $A_1$ sites in the topaz crystal. This conclusion is based on the following properties of the observed spectra:

(a) Only two sets of lines are observed for rotations about crystal axes.

(b) When the magnetic field is directed along a crystal axis, both of the sets of lines mentioned in (a) coincide.

(c) For the magnetic field direction not in either the $[100]$, $[010]$ or $[001]$ crystal planes, the spectrum consists of four sets of lines.

These observed properties of the spectra in topaz are just those which would be expected if the paramagnetic centers are at $A_1$ sites in the crystal.
As was mentioned before, the immediate surroundings of an Al ion in the crystal consists of four oxygens and two fluorines. The fluorine nucleus has a nuclear spin \( I = 1/2 \). The hyperfine structure can be explained by assuming that the paramagnetic centers are at Al sites and that each center couples equally with each nearest neighbor fluorine nucleus.

Although the site of the paramagnetic center in the crystal has been located, the paramagnetic center itself has not been identified. It would be reasonable to suspect that since Cr and Fe impurities are present in the crystal, the spectrum might be due to Cr\(^{+++}\) or Fe\(^{+++}\) at Al sites. However, the observed spectrum is not characteristic of these ions. In the case of Cr\(^{+++}\) or Fe\(^{+++}\) one would expect to observe fine structure lines characteristic of these ions. The observed spectrum for the paramagnetic center consists of only a single hyperfine triplet and it is difficult to imagine how Cr\(^{+++}\) or Fe\(^{+++}\) could give such a spectrum. The paramagnetic center is probably not a trapped electron for the effective \( g \) values of the resonances are in the range 3.5 to 4.5 which is not characteristic of an almost free electron.
Figure 19

The first derivative record of the paramagnetic resonance of one hyperfine triplet in the spectrum of topaz is shown. The magnetic field direction is not in the \([100]\), \([010]\) or \([001]\) crystal planes but in some other direction relative to the crystal. The microwave frequency was 8950 Mc./sec.
An attempt was made to explain the spectrum in terms of a phenomenological spin Hamiltonian of the form

$$\mathcal{H}_J = \beta [g_x H_x S_x + g_y H_y S_y + g_z H_z S_z] + A \mathbf{I} \cdot \mathbf{S}$$

with $S = 1/2$ and $I = 1$, but as was mentioned in the previous chapter the observed spectra are in disagreement with such an assumption.
CHAPTER VII

PARAMAGNETIC RESONANCE INVESTIGATIONS ON LYOPHILIZED CHLORELLA CONTAINING MANGANESE

It is a well known fact\textsuperscript{31} that manganese is an essential nutrient for algae. The actual role of manganese in algae is not completely understood at the present. A proposal was made by researchers at the Charles Kettering Foundation that a possible clue to the role of manganese in algae might be obtained if electron paramagnetic resonance could be used to establish the valence state of the manganese in Chlorella. Manganese is paramagnetic in all valence states except the $+7$ state; hence, it was hoped that the paramagnetic resonance of manganese in algae might be observed.

In principle, the valence state of a paramagnetic ion in a chemical system can be determined by electron-spin-resonance techniques. In practice whether or not such a determination can be made usually depends on whether a single crystal of the chemical system can be obtained. When a single crystal which is suitably dilute in the paramagnetic ion and which has a crystalline or

molecular electric field of lower symmetry than cubic at the paramagnetic ion can be obtained, the valence state of a given paramagnetic ion can be determined by observing the number of fine structure lines which are present in the spectrum. This is due to the fact that the number of fine structure lines depends on the total spin S of the ion which in turn depends on the valence state of the ion. If one has the misfortune of dealing with a polycrystalline system in which the symmetry of the crystalline or molecular field is lower than cubic, then observation of the resonance spectrum is unlikely because orientation averaging will produce a very broad absorption line which is extremely difficult to observe experimentally in dilute systems.

In the case when only polycrystalline samples are available one may hope that the crystalline or molecular field at the paramagnetic ion has spherical symmetry. For such a situation, manganese with nuclear spin I = \( \frac{3}{2} \) would be expected to give six rather narrow hyperfine-structure lines. If the number of manganese ions in the sample is known from a chemical analysis, then the valence state of the manganese can be determined by measuring the total amount of power absorbed by the sample and comparing it with the power absorbed by another sample which contains a known number of paramagnetic ions with a known valence state. This is a possible method because the
total power absorbed by a paramagnetic ion in a resonance experiment depends on the number of ions present and the total spin $S$ of the ions.

Paramagnetic resonance experiments on lyophilized Chlorella have been carried out with the intention of gaining some information on the valence state of manganese in this biological system. The samples of lyophilized Chlorella supplied by the Charles Kettering Foundation were in the form of a powder. Experiments were performed on the powder and it was found that 0.1 grams of the Chlorella gave no observable resonance absorption. At this point no information on the amount of manganese in the Chlorella was available. The next experiment carried out was one in which a 0.5 gram sample of Chlorella was ashed and treated with an $\text{H}_2\text{SO}_4$ solution and zinc for the purpose of reducing any manganese in the ashed sample to the +2 valence state. This solution was filtered and an attempt to observe the $\text{Mn}^{++}$ resonance in the solution was made with no success. A spectrographic analysis by Dr. Howard Bales of the Kettering Foundation showed that the manganese content of the Chlorella was approximately 40 p.p.m. by weight. It should be mentioned at this point that if the manganese in the powder was in a crystalline environment of spherical symmetry the 0.1 grams of Chlorella would have given an observable resonance unless it was in the +7 valence state. This concentration
of manganese in the Chlorella was not sufficient to give an observable resonance in the second experiment because to observe the Mn$^{++}$ resonance in water solutions only sample volumes of 0.1 cc. can be used. One is restricted to such small samples because the high dielectric loss of water reduces the Q of the microwave cavity. From the results of the experiment on the powder it was concluded that the valence state of manganese in Chlorella could probably not be determined.

Some additional experiments which were carried out gave rather interesting results. It was observed, that when lyophilized Chlorella was added to a known solution of MnCl$_2$•4H$_2$O in water, a considerable amount of manganese was taken out of solution by the Chlorella. This was determined by comparing the intensity of the manganese resonance lines of 0.1 cc. of a 0.005 molal MnCl$_2$•4H$_2$O solution, before the Chlorella was added, to the intensity of the manganese resonance of 0.1 cc. of this same solution after the Chlorella was added. It was observed that the widths of the lines in the resonance spectrum of Mn$^{++}$ in this 0.005 molal solution, to which the Chlorella was added, were within the experimental error equal to the widths of the lines in the 0.005 molal solution to which no Chlorella was added. The measurements on the widths of the Mn$^{++}$ resonance spectrum of MnCl$_2$•4H$_2$O solutions
by Paul Gordon\textsuperscript{32} show that the line widths of the Mn\textsuperscript{++} hyperfine lines in these solutions are approximately constant for solutions below 0.1 molal. Hence the intensity of absorption of MnCl\textsubscript{2}·4H\textsubscript{2}O water solutions below 0.1 molal is expected to be a linear function of the concentration; this is actually observed experimentally. Because the widths of the Mn\textsuperscript{++} resonance lines were unchanged when lyophilized Chlorella was added to a 0.005 molal MnCl\textsubscript{2}·4H\textsubscript{2}O solution and only the intensity decreased, it was inferred that the Mn\textsuperscript{++} was being taken out of solution and bound to the Chlorella in some manner. The conclusion here is that once the manganese was bound to the algae it gave an extremely broad resonance which could not be observed. The results of such experiments for a 0.005 molal solution to which various amounts of Chlorella have been added are shown in Fig. 20. In Fig. 20, \(N\) is the amount of manganese in solution before the Chlorella is added and \(t\) is the amount of manganese which gives an observable resonance spectrum after the Chlorella is added to the solution. Thus from these measurements which are summarized in Fig. 20 the relationship \[
\frac{N}{t} = KC + 1
\] appears to exist. \(K\) is a constant and \(C\) is the concentration of Chlorella added to a given amount of a 0.005 molal
MnCl$_2$-4H$_2$O water solution. The similarity between this effect of adding Chlorella to a MnCl$_2$-4H$_2$O water solution and the effect of adding a complexing agent to a MnCl$_2$-4H$_2$O water solution is shown in Fig. 21. In the experiments with the complexing agent E.D.T.A.D. (Ethylene-dinitrilo tetracetic acid disodium salt), it was again observed that on adding the complexing agent to the solution the widths of the Mn$^{++}$ hyperfine structure lines did not change, only the intensity of the absorption decreased. This again indicated Mn$^{++}$ was being taken out of solution by the complexing agent. Townsend and Cohn$^{33}$ have observed


this same effect for other complexing agents. The results given in Fig. 21 can be understood by postulating that, in the MnCl$_2$-4H$_2$O water solution with complexing agent present, one has a reaction of the type

$$\text{Mn}^{++} + (X)^{-2} \rightleftharpoons \text{MnX}$$

(7.1)

where $(X)^{-2}$ is the divalent complex negative ion. For such a reaction the equilibrium relation is given by the expression

$$K = \frac{C(\text{Mn}^{++})}{C(\text{X}^{-2})} \cdot \frac{C(\text{MnX})}{C(\text{Mn}^{++})}$$

(7.2)
Figure 20

A plot of $N/t$ vs. grams of Chlorella added to 100 ml. of a 0.005 molal $\text{MnCl}_2\cdot4\text{H}_2\text{O}$ solution is shown. $N$ is the amount of $\text{Mn}^{++}$ in solution before the Chlorella is added and $t$ is the measured amount of $\text{Mn}^{++}$ in solution after the Chlorella is added. In this case $N$ is constant and is 0.005 moles/liter of solution.
Grams of Chlorella in 100 ml. of a 0.005 Molal Solution
where \( K \) is defined to be the dissociation constant of the MnX complex and \( C(\text{Mn}^{++}) \) is the concentration of \( \text{Mn}^{++} \) in solution. If one postulates this type of reaction as occurring, then from the results summarized in Fig. 21, \( K \) calculated for the complex formed by adding E.D.T.A.D. to a \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \) solution is found to be \( K = 1.3 \pm 0.2 \times 10^{-2} \) moles/liter. A similar experiment in which \( \text{NH}_4\text{H}_2\text{PO}_4 \) was added to the \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \) solution was suggested by Professor R. C. Nelson. The results of this experiment are shown in Fig. 22. In this case the \( \text{NH}_4\text{H}_2\text{PO}_4 \) does not remove \( \text{Mn}^{++} \) from solution as was observed for E.D.T.A.D.

In the course of the previous experiments it was discovered that if an acid is added to a \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \) water solution, the intensity of the resonance signal decreases, the line width remaining unchanged, as the percentage of acid in solution is increased while the molarity of \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \) is held constant. The results of these experiments are shown in Figs. 23, 24 and 25. The effect is most pronounced for the strong acids and less pronounced for the case of a weak acid. At present this acid effect on the \( \text{Mn}^{++} \) resonance in water solutions is not understood.
Figure 21

A plot of $N/t$ vs. concentration of E.D.T.A.D. in a 0.05 molal $\text{MnCl}_2\cdot4\text{H}_2\text{O}$ solution is shown. $N$ is the amount of $\text{Mn}^{++}$ in solution before the E.D.T.A.D. is added and $t$ is the measured amount of $\text{Mn}^{++}$ in solution after the E.D.T.A.D. is added. In this case $N$ is constant and is 0.05 moles/liter of solution.
Molal Conc. of E.D.T.A.D. in a 0.05 Molal MnCl₂·4H₂O Solution
Figure 22

A plot of N/t vs. concentration of NH$_4$H$_2$PO$_4$ in a 0.05 molal MnCl$_2$·4H$_2$O solution is shown.
Molal Conc. of $\text{NH}_4\text{H}_2\text{PO}_4$ in a 0.05 Molal $\text{MnCl}_2\cdot4\text{H}_2\text{O}$ Solution
Figure 23

A plot of the relative intensity of absorption of the Mn$^{++}$ resonance vs. volume concentration of H$_2$SO$_4$ in the solvent of a 0.015 molal MnCl$_2$·4H$_2$O solution is shown.
% Conc. (by volume) of H₂SO₄ in Solvent
Figure 2

A plot of the relative intensity of absorption of the Mn$^{++}$ resonance vs. volume concentration of HCl in the solvent of a 0.015 molal MnCl$_2$·4H$_2$O solution is shown.
Rel. Int. of Mn$^{+}+$ Absorption vs. % Conc. (by volume) of HCl in Solvent
Figure 25

A plot of the relative intensity of absorption of the Mn$^{++}$ resonance vs. volume concentration of Acetic Acid in the solvent of a 0.015 molal MnCl$_2$·4H$_2$O solution is shown.
Rel. Int. of Mn^{2+} Absorption

% Conc. (by volume) of Acetic Acid in Solvent
CHAPTER VIII

AN ATTEMPT TO OBSERVE THE PARAMAGNETIC RESONANCE OF
OPTICALLY EXCITED TRIPLLET STATES
IN ORGANIC PHOSPHORS

One of the outstanding problems in the spectroscopy of complex organic molecules has been the nature of the metastable excited state, responsible for phosphorescence observed in these molecules. As a result of spectroscopic studies by Lewis and Kasha\textsuperscript{34,35}, this phenomenon has been interpreted as a lowest triplet to singlet emission. The phosphorescence has been interpreted by Lewis and Kasha in the following manner. Consider the energy level scheme given in Fig. 26 where $S$ and $S'$ are the two lowest singlet states in the molecule and $T$ is the lowest triplet state. The phosphorescent or triplet state $T$ is reached by absorption of energy by the molecule via the transition $S \rightarrow S'$ followed by a non-radiative transition $S' \rightarrow T$. Phosphorescence is ascribed to the emission $T \rightarrow S$. The lifetime in the singlet state

\textsuperscript{34}G. N. Lewis and M. Kasha, J. Am. Chem. Soc. \textbf{66}, 2100 (1944).

The lowest three energy levels in an organic phosphor are shown. In the plot $S$ and $S'$ are the two lowest singlet states and $T$ is the lowest triplet state; $F$ refers to the transition which gives rise to fluorescence and $P$ to the transition which gives rise to phosphorescence.
Non-Radiative Transition
S' is short compared to the lifetime in the state T because electric dipole transitions are allowed for the singlet-singlet transition and forbidden for the triplet-singlet transition. The intervention of spin-orbit coupling brings about a mixing of singlet and triplet states, destroying their purity, and thereby permitting transitions between nominal singlet and triplet states to be observed.

The most important experimental verification of this explanation was the photomagnetism observed by Lewis, Calvin and Kasha\textsuperscript{36} during intense irradiation of fluorescein in a boric acid glass. The photomagnetism was observed by bulk susceptibility measurements. Similar and more conclusive measurements have been made by Evans,\textsuperscript{37} who has been able to show that for triphenylene in boric acid glass the mean lifetime of the photomagnetism is the same as the mean lifetime of the phosphorescence.

Because of this fairly conclusive evidence that the metastable state in organic phosphors was a triplet state, an attempt has been made to detect the paramagnetic resonance absorption of this metastable state. A variety of phosphors in a microwave cavity were irradiated with light...
from a high pressure mercury arc. The method of irradiating the phosphors while in the cavity is shown in Fig. 27. In the first series of experiments the phosphors investigated were those in which Evans observed photomagnetism. The following samples have been investigated both at 300°K and at 80°K, over a concentration range of about $10^{-2}$ to $10^{-4}$ molar:

(a) Acid fluorescein, acridine orange and triphenylene in boric acid glasses.

(b) Triphenylene in organic solvents (ether pentane-alcohol, methyl cyclohexane and 3-methyl pentane) at 80°K.

In all of these phosphors the $S \rightarrow S'$ absorption was in the visible region of the optical spectrum and the lifetimes of the phosphorescent state were greater than two seconds. In all of these samples it was estimated, from a knowledge of the intensity of the high pressure mercury arc and the size of the samples used, that a steady state concentration of more than $10^{15}$ triplet state molecules was formed. This concentration would have been easily detected, unless the resonance line was much broader than 100 gauss. None of the samples showed an electron paramagnetic resonance which could be associated with photo-excited triplet states.
Figure 27

The method used to irradiate the organic phosphor samples at 80°K while in a microwave cavity is shown.
Method of Irradiating Phosphor Samples
At 80° K
Boric acid glasses containing triphenylene or fluorescein exhibited photo-decomposition when excited by ultraviolet radiation; the products (blue and brownish in color, respectively) were identified as free radicals by their strong spin resonance absorption. In the case of the radical formed from triphenylene, the resonance line had a g value of $2.006 \pm 0.002$, and a halfwidth of 3 gauss. Gentle heating of the glass was found to destroy both the color and the resonance absorption; presumably the radicals recombined with their electrons, which diffused to them from the lattice. No radicals were formed by ultraviolet irradiation of triphenylene dissolved in organic solvent glasses at $80^\circ$K.

It was conjectured at this point that probably the spin-orbit interaction, which is responsible for the emission $T \rightarrow S$, combined with crystalline fields at the organic molecules was preventing detection of the paramagnetic resonance. The combined effect of the spin-orbit interaction and a crystalline electric field of symmetry lower than cubic would remove in zero magnetic field some of the degeneracy of the spin states, as was discussed in Chapter I. Since probably all the organic molecules in the glass are not subjected to the same crystalline electric field and since there is a random orientation of the crystalline electric fields with respect to the externally applied magnetic field, it would be expected that the
resonance absorption would be very broad. This broadening would come about due to a "smearing" of the fine structure lines over all orientations of the crystal with respect to the magnetic field.

A further experiment was then performed in which single crystals of the phosphor dibenzothiophene were investigated. In this case one would not have the complication of orientation averaging of the fine structure spectrum, as would occur in the glasses. However, even in these single-crystal phosphor samples no resonance was observed at 300°K or at 80°K. If it is assumed that greater than $10^{15}$ triplet molecules in the sample were produced by the irradiation then the negative results in this case would seem to indicate that either spin-lattice relaxation mechanisms were responsible for broadening of the resonance lines or the Stark splitting of the triplet levels due to spin-orbit interaction in this crystal is much larger than the microwave quantum.

While no workers have published results of this type of experiment, it has been learned through private communications that similar negative results have been obtained by C. A. Hutchison (University of Chicago), D. J. E. Ingram (University of Southhampton) and some Russian workers. All of these investigators seem to agree
that either spin-lattice relaxation broadening or large Stark splittings of the triplet state have prevented observation of magnetic resonance absorption in photo-excited triplet states.
CHAPTER IX

PARAMAGNETIC RESONANCE STUDY OF IRRADIATION DAMAGE IN POLYCRYSTALLINE CARBOHYDRATES

Discussion

By subjecting organic molecules in solids to strongly ionizing radiation such as X-rays and \( \beta \)-rays, electrons can be removed from ground state molecular orbitals with sufficient energy to free them from the molecule. When the organic molecule loses an electron in this manner, the ionized molecule, if it holds together, will have an unpaired electron in one of its orbitals. The electron which is removed from one molecule may become attached to a neighboring molecule and go into an excited orbital of this molecule or it may be trapped at imperfections in the crystal lattice. It is possible for the ionizing radiation to produce either positively or negatively charged radicals. The paramagnetic resonance studies which will be discussed later cannot distinguish between these two possible types of radicals. In most cases the formation of the radicals will be a complicated process in which the ionizing radiation produces unstable radicals which in turn will decay to other radicals until a stable radical is formed. If the barrier to the return passage of the electrons between the molecules is large, then sufficiently high concentrations
of free radicals can be built up to give a detectable electron-spin resonance.

If the spin of the unpaired electron in the radical is entirely free from the perturbing influence of its environment, a single sharp line with \( g = 2.0023 \) might be expected. However, the electron is very sensitive to its environment and information about the interaction of the electron with its surroundings can usually be obtained from the paramagnetic resonance spectrum. In the resonance spectrum there are usually two sources of information. The most important source of information is the hyperfine structure which arises from the interaction of the magnetic moment of the electron with the magnetic moments of the nuclei on which the electron is localized. A second source of information is the small residual spin-orbit coupling which in some cases causes the \( g \)-factor to be slightly anisotropic and different from the free-spin value.

Hyperfine structure.—The hyperfine structure splittings in polyatomic free radicals have been discussed in detail by Weissman.\(^{38}\) If the interaction of the electron

constant frequency are given by

\[ H = \left( \frac{\hbar \nu}{g \beta} \right) + \frac{1}{g \beta} \sum_i A_i m_i \]  \hspace{1cm} (9.1)

\( A_1 \) is the coupling constant of the electron with a particular nucleus \( i \) with spin \( I_1 \) and the magnetic quantum numbers have the values \( m_1 = I_1, I_1 - 1, \ldots, -I_1 \).

If all the coupling nuclei in a given free radical have the same coupling \( A_1 \) to the electron spin, one can define

\[ T = \sum I_1 \]  \hspace{1cm} (9.2)

and a total magnetic quantum number \( M = T, T-1, \ldots, -T \). For this situation (9.1) can be written in the simpler form

\[ H = \left( \frac{\hbar \nu}{g \beta} \right) + \left( \frac{A_1}{g \beta} \right) M \]  \hspace{1cm} (9.3)

In this case the spectrum consists of \((2T + 1)\) components each separated by \( \Delta H = \left( \frac{A_1}{g \beta} \right) \). The intensities of the components are proportional to the number of different combinations of \( m_1 \)'s which give the same value of \( M \).

The interaction constant \( A_1 \) of the electron spin with the moment of a particular nucleus \( i \) in general contains both an isotropic component and an anisotropic component. The isotropic component, which is the Fermi term, is independent of the orientation of the magnetic field and arises from the non-vanishing of the electronic wave function at the nucleus in question. Since only the s atomic orbitals are non-vanishing at the nucleus, the presence of
an isotropic coupling term for a particular atom in a molecule, generally indicates the s character in the bonding orbitals of the atom. The anisotropic contribution to $A_i$ comes from the direct magnetic dipole-dipole coupling of the electron with the nucleus i. In a single crystal one can distinguish between the isotropic and anisotropic contributions to $A_i$ by studying the hyperfine separations as the crystal is rotated with respect to the external magnetic field. For polycrystalline samples, one cannot in general distinguish between the isotropic and anisotropic terms. Instead an average $A_i$ is obtained, because in a polycrystalline system the chemical bond axes are randomly oriented with respect to the magnetic field.

**g-anisotropy.**—When the unpaired electron is localized on a non-s orbital of a single atom of a radical, the effects of spin-orbit interaction cannot be neglected. The orbital angular momentum is oriented by the strong electrical forces of the chemical bond and this gives rise to an anisotropy in the g factor. If the electron wave function is symmetric about a chemical bond, the g factor reflects this symmetry. For an arbitrary orientation $\theta$ of the bond axis with respect to the external magnetic field, the observed g factor is given by

$$g^2 = g_{||}^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta.$$  

(9.4)
In the case of a polycrystalline sample, the resonance absorption is averaged over all possible orientations of the bond axis with respect to the magnetic field. Since the $g_{\perp}$ value has greater weight than $g_{\parallel}$, the resonance has an asymmetric shape with two peaks. The peak with maximum intensity corresponds to the $g_{\perp}$ value and the other peak corresponds to $g_{\parallel}$.

In a polycrystalline sample one can distinguish between hyperfine structure effects and effects due to $g$ anisotropy by studying the spectrum at several different frequencies. Once the strong-field or Paschen-Back case, which we have assumed before, is realized, the hyperfine structure separation is independent of the frequency of observation. The effect due to $g$ anisotropy depends on the frequency of observation.

**Experimental Results**

The electron paramagnetic resonance study of radiation damage to organic molecules has been pursued by a large number of workers. Gordy and co-workers\textsuperscript{39,40,41,42,43,44} have carried out paramagnetic resonance studies on

\begin{itemize}
  \item \textsuperscript{40}G. McCormick and W. Gordy, Bull. Am. Phy. Soc. \textbf{1}, 200 (1956).
\end{itemize}
free radicals produced by X-irradiation of amino acids, peptides, fatty acids, nucleic acids, proteins, enzymes, hormones and vitamins. In the remainder of this chapter, the results of similar studies on X-irradiated and $\beta$-irradiated carbohydrates are reported.

A total of seventeen irradiated carbohydrates have been studied by observing the paramagnetic resonance spectra of polycrystalline samples of these materials. $\delta$-Glucose, $\delta$-glucitol, $\delta$-galactose, and inositol have been studied after irradiation with both X-rays and $\beta$-rays. In each of these samples the paramagnetic resonance spectrum of the X-irradiated sample was identical with the spectrum of the $\beta$-irradiated sample. This result seems to indicate that the final radical products produced by X-irradiation are the same as those produced by $\beta$-irradiation.

In most of the irradiated carbohydrates which have been studied, the spectra consist of a number of overlapping lines. To analyze the spectrum of an irradiated sugar which is composed of overlapping lines it is necessary to be careful in identifying the positions of absorption lines. For the purpose of deciding on the position of a line in
the spectrum it is usually necessary to integrate the first derivative of the absorption spectra. It is to be recalled that because of the particular experimental methods used, the recorded traces are actually first derivatives of the absorption lines. In the figures to be presented the apparent position of lines are located, since maxima and points of inflection of the absorption curve are easily identified on the first derivative traces.

Irradiated d-glucose, d-fructose, lactose, \( \ell \)-sorbose, \( \ell \)-arabinose and d-galactose give very similar paramagnetic resonance spectra. The spectra of these irradiated sugars are shown in Figs. 28, 29 and 30. The spectra of each of these samples show a characteristic four-line hyperfine structure with an average spacing between lines \( (A/g\beta) \) of approximately 15 gauss. The g factor which is calculated from the center of the spectrum is \( 2.003 \pm 0.001 \). For d-fructose and lactose the hyperfine structure is best resolved and a detailed investigation of the spectra indicates that the hyperfine structure components have an intensity ratio of 1:3:3:1. This type of hyperfine structure is to be expected if the electron is interacting with three protons (\( I = 1/2 \)) for each of which \( (A/g\beta) = 15 \) gauss.

The hyperfine structure observed for \( \ell \)-sorbose and \( \ell \)-arabinose are not as well resolved as for d-fructose and lactose, but the position of the hyperfine lines coincide with those observed in d-fructose and lactose. For d-galactose
Figure 28

First derivative curves of $\beta$-irradiated d-fructose and X-irradiated lactose are shown.
Figure 29

First derivative curves of X-irradiated \( \alpha \)-sorbose and \( \alpha \)-arabinose are shown.
Figure 30

First derivative curves of X-irradiated d-galactose and $\beta$-irradiated d-glucose are shown.
and d-glucose the hyperfine structure is barely resolved. In d-galactose only the two outermost lines can be located with reasonable accuracy; however, the position of these two outermost lines is almost the same as those observed in d-fructose. For d-glucose the four-line hyperfine structure is observed, but for this sugar two additional lines are observed near the center of the hyperfine pattern; this probably indicates that for this sugar more than one stable radical has been formed.

From the paramagnetic resonance spectrum alone it is difficult to obtain a unique identification of the radical responsible for the hyperfine structure observed in d-glucose, d-fructose, lactose, L-sorbose, L-arabinose, and d-galactose. However, the magnetic resonance spectra indicate that possible radicals are limited to types which contain three equally coupling protons.

The paramagnetic resonance spectra observed for ir-radiated erythritol, d-threitol, rhamnose and inositol are shown in Figs. 31 and 32. For erythritol and d-threitol the spectrum consists of two lines of equal intensity. This type of spectrum would be expected if the electron were interacting with a single proton in the radical. The hyperfine spacing (A/g\(\beta\)) for erythritol and d-threitol is approximately 6 gauss. The hyperfine structure is centered on \(g = 2.003 \pm 0.001\). Two lines of equal intensity are observed in the rhamnose spectrum also; these two
lines are assumed to be a hyperfine doublet with \((A/g\beta) = 6\) gauss and \(g = 2.002 \pm 0.001\). In the inositol spectrum four lines are observed. These four lines consist of a pair of intense lines and two weak lines. If the two strong lines in the spectrum, labeled A and C in Fig. 32, are associated with a hyperfine doublet, then \((A/g\beta)\) for this pair of lines is 25 gauss. The center of this assumed hyperfine structure doublet is at \(g = 2.002 \pm 0.001\). If the weaker pair of lines are also considered a hyperfine structure doublet, then \((A/g\beta)\) for this set of lines is 19 gauss and \(g = 1.991 \pm 0.001\).

In the carbohydrates thus far discussed, the only nuclei with non-zero nuclear spins were protons. In Fig. 33 is shown the magnetic resonance spectrum of irradiated glucosamine. In addition to protons glucosamine contains one nitrogen atom. For \(N^{14}\) the nuclear spin \(I = 1\). The spectrum of glucosamine shows five lines with an over-all separation between outermost lines of 74 gauss. The center of this five-line structure is at \(g = 2.001 \pm 0.001\). An analysis of this spectrum indicates that the spectrum consists of five equally spaced lines separated by 18.5 gauss. The spectrum can possibly be interpreted as hyperfine structure due to the electron coupling equally with four protons. Another possibility is that the spectrum is due to the electron coupling equally with two protons and a nitrogen. For four protons coupling equally to the electron the...
Figure 31

First derivative curves of X-irradiated d-threitol and erythritol are shown.
Figure 32

First derivative curves of X-irradiated rhamnose and inositol are shown.
Magnetic Field (Gauss)

$\nu = 9267.3 \text{ Mc/sec}$

Rhamnose

Magnetic Field (Gauss)

$\nu = 9270.4 \text{ Mc/sec}$

Inositol
Figure 33

The first derivative curve of X-irradiated glucosamine is shown. (Note: The compound referred to in the text as glucosamine is actually glucosamine hydrochloride.)
Magnetic Field (Gauss)

\[ \nu = 9267.0 \text{ Mc/sec.} \]

Glucosamine Hydrochloride

\[
\text{CHO} \quad \text{CH}(\text{NH}_2\text{Cl})
\]

\[
\text{HO} - \text{C} - \text{H} \\
\text{H} - \text{C} - \text{OH} \\
\text{H} - \text{C} - \text{OH} \\
\text{CH}_2\text{OH}
\]
expected intensity ratio of the lines would be 1:4:6:4:1, whereas for the electron coupling equally to two protons and a nitrogen the intensity ratio of the lines would be 1:3:4:3:1. One other possibility is that the spectrum is due to the electron coupling equally with two nitrogens for which case the expected intensity ratio of the lines would be 1:2:3:2:1. To aid in making an estimate of the relative intensities of the five lines in the glucosamine spectrum, the first derivative record given in Fig. 33 was integrated. An estimate of the intensities was made by trying to reproduce the observed spectrum from five lines of equal width but different peak heights. Only a very crude estimate could be made because of the large amount of overlap of the lines, but this crude analysis seemed to indicate that the ratio of the relative intensities was approximately 1:3:4:3:1. If the spectrum is actually due to the electron coupling equally with two protons and a nitrogen, the fact that the coupling constant for the proton is identical with the coupling constant for the nitrogen is an unexpected and surprising result.

The spectra observed for irradiated d-glucitol and d-xylose are shown in Fig. 34. Each of these samples showed only a single absorption line with no hyperfine structure. The line observed in d-glucitol has $g = 2.002 \pm 0.002$. The spectrum observed in xylose is asymmetrical and appears to be composed of a single sharp line with $g =$
2.003 ± 0.001 which is superimposed on a much broader line.

In Fig. 35 the spectra observed for irradiated pentaerythritol and d-mannitol are shown. For each of these samples the spectrum is complex. In both spectra there is evidence that the quartet observed in d-fructose is present; however, additional lines which are present prevent the quartet from being identified with certainty. In both sugars the apparent positions of lines are indicated in the figures.

Irradiated d-mannose and sucrose have also been studied and the spectra of these sugars are shown in Fig. 36. The d-mannose spectrum consists of three absorption peaks which can be associated in several ways. If peak A and B are associated with a hyperfine doublet, then for this pair of lines \((A/g \beta) = 12\) gauss and \(g = 2.002 \pm 0.001\). Another possibility is that A is a single sharp line with \(g = 2.006 \pm 0.001\) and that B and C are lines in a hyperfine triplet with the third line unresolved because of its overlap with line A. Assuming that B and C are lines in a hyperfine triplet with possible intensity ratio 1:2:1, then \((A/g \beta)\) is approximately 15 gauss and \(g = 1.999 \pm 0.001\). To distinguish between these various possibilities for d-mannose, it would be necessary to study the paramagnetic resonance spectrum of this sugar at a higher microwave frequency. The spectrum observed for sucrose is complex and the possible
Figure 34

First derivative curves of X-irradiated d-glucitol and d-xylose are shown.
Figure 35

First derivative curves of β-irradiated pentaerythritol and d-mannitol are shown.
Figure 36

First derivative curves of $\beta$-irradiated d-mannose and sucrose are shown.
positions of peaks are indicated in Fig. 36. The center of the sucrose spectrum is at \( g = 2.002 \pm 0.001 \).

**Conclusions**

In most of the irradiated carbohydrates studied, the existence of hyperfine structure in the paramagnetic resonance spectrum suggests the general nature of the radical produced by the radiation. From a consideration of the chemical structure of some of these sugars, some of the similarities observed in the spectra of different sugars are not surprising.

For d-glucose and d-galactose the structures are given below.

\[
\begin{align*}
\text{d-Glucose} & \quad \text{d-Galactose} \\
\text{H} & \quad \text{H} \\
\backslash & \quad \backslash \\
\text{C} & = \text{C} \\
\text{=} & \quad \text{=} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{C} & \text{OH} \\
\text{H} & \quad \text{H} \\
\text{C} & \text{OH} \\
\text{H} & \quad \text{H} \\
\text{C} & \text{OH} \\
\text{CH}_2\text{OH} \\
\end{align*}
\]

The only difference in structure of these two sugars is the relative position of one OH group. Hence, since there is such a great similarity in the structure of these two sugars, it is not surprising that the radicals produced by irradiation of these molecules would give similar paramagnetic resonance spectra.
In d-fructose and $\alpha$-sorbose again the only difference in structure is the relative position of one OH group; hence, it is not surprising that the spectra of each of these irradiated sugars are similar. The structures of d-fructose and $\alpha$-sorbose are given below.

\[
\begin{align*}
\text{d-Fructose} & \quad \text{CH}_2\text{OH} \\
& | \\
& C = O \\
& | \\
& \text{HO - C - H} \\
& | \\
& \text{H - C - OH} \\
& | \\
& \text{H - C - OH} \\
& | \\
& \text{CH}_2\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{\alpha-Sorbose} & \quad \text{CH}_2\text{OH} \\
& | \\
& C = O \\
& | \\
& \text{HO - C - H} \\
& | \\
& \text{H - C - OH} \\
& | \\
& \text{HO - C - H} \\
& | \\
& \text{CH}_2\text{OH}
\end{align*}
\]

The spectra of erythritol and d-threitol were found to be similar and again the only difference in structure of these two is the relative position of an OH group. Their structures are shown below.

\[
\begin{align*}
\text{Erythritol} & \quad \text{CH}_2\text{OH} \\
& | \\
& \text{H - C - OH} \\
& | \\
& \text{H - C - OH} \\
& | \\
& \text{CH}_2\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{d-Threitol} & \quad \text{CH}_2\text{OH} \\
& | \\
& \text{HO - C - H} \\
& | \\
& \text{H - C - OH} \\
& | \\
& \text{CH}_2\text{OH}
\end{align*}
\]
There are exceptions to this proposed association of similarity in structure with similarity in observed spectra. For example, d-glucitol and d-mannitol are different only in the relative position of one OH group and yet the paramagnetic resonance spectra of these are different. The compounds l-arabinose and d-xylose also differ only in the relative position of one OH group, and again the spectra observed are different. Mr. Leo McCabe, who prepared and purified the samples, has found that the sample of l-arabinose contained approximately 1 per cent of d-galactose. However, it is felt that probably such a small amount of galactose in the arabinose cannot account for the difference observed in the paramagnetic resonance spectra of irradiated l-arabinose and d-xylose.

Many questions about the effects of radiation damages to carbohydrates and the free radicals produced are still unanswered. However, it is hoped that the results of the paramagnetic resonance studies which have been carried out can be used in helping decide what radicals are formed by the ionizing irradiation. On the basis of the present work further studies seem justified. The study of irradiated single crystals of carbohydrates would probably yield additional information.

A very simple and probably enlightening experiment would be to study a number of irradiated cyclitols (inositol is one of these) to determine the effect of stereoisomerism on the radicals produced.
Bibliography


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