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An electron spin resonance study of divalent manganese in cordierite.

Onuekwusi Obinabo

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AN ELECTRON SPIN RESONANCE STUDY
OF DIVALENT MANGANESE
IN CORDIERITE

By

Onuekwusi Obinabo

A Thesis
Submitted to the Faculty of Graduate Studies through the
Department of Physics in Partial Fulfillment
of the Requirements of the Degree of
Master of Science
University of Windsor

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April 1968
Approved by

Dr. N. E. Hedgecock

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Dr. R. J. Thibert

201624
ABSTRACT

The electron spin resonance of Mn$^{2+}$ in a single crystal of cordierite has been investigated using X-band frequency at room temperature ($300^\circ$K) and at liquid nitrogen temperature ($77^\circ$K). The spectrum was interpreted as that of Mn$^{2+}$ ions which substitutionally replace Mg. The spectra showed the usual hyperfine structure. The spectrum can be described by a spin Hamiltonian of orthorhombic symmetry whose constants were found to have the following values: $b_2^0 = 422.1$ (432.1), $b_2 = 26.5 (18.4)$, $b_4^0 = -4.3 (-4.8)$, $b_4 = -12.9 (3.2)$, $b_4^4 = -23.3 (-14.5)$, $A = -89.9 (-89.2)$, $B = -88.6 (-93.5)$, $C = -89.4 (-92.0)$, 
$g_x = 1.9981 (2.0019)$, $g_y = 1.9971 (1.9977)$, $g_z = 1.9969 (1.9962)$. The values in brackets correspond to liquid nitrogen temperature results. The crystalline field parameters and the hyperfine constants are expressed in gauss.
ACKNOWLEDGEMENTS

The author gratefully thanks Dr. N. E. Hedgecock for his help and encouragement during the course of the research.
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CHAPTER I
INTRODUCTION

A. Historical Introduction and Basis for ESR

Electron spin resonance (ESR) is one of several magnetic resonance phenomena which have become useful as a means of physical investigation. ESR is observable from electrons in an unpaired and therefore paramagnetic state. Electron paramagnetism occurs in the following materials: materials containing atoms of the transition elements with incomplete inner shells, as in the case of the iron or rare earth groups; conduction electrons in metals; ferro- and ferrimagnetics; imperfections in insulators which may trap electrons or holes as in the case of the F-center (electron trapped at the site of a missing halogen ion in an alkali halide), or donor and acceptor sites of semiconductors.

This resonance absorption by the unpaired electron was discovered by Zavoyskiy in 1945. Notable among the early workers in the field was Gorter who used a calorimetric method to measure the energy change. A comprehensive bibliography to the historical development of the phenomenon is given in Al'tshuler (1964).
After the experiments carried out by Zavoyskiy, the newly found field has found great applications in different fields of science - notably in the fields of solid state physics, where it has been used for example in the study of crystalline fields around trace impurities in the host crystals; in engineering, where for example it can provide information on the impurity concentration in semi-conductors; in chemistry and biology for chemical and biological studies (Waters et al., 1968). 

It is however, important to note that the possession of a free electron is not sufficient to ensure resonance. This can be seen by considering the sodium atom. It has zero orbital magnetic moment and angular momentum, but has however a spin of $\frac{1}{2}$ and corresponding spin magnetic moment. The magnetic moment can be studied by the method of atomic beams. In sodium metal, the valence electrons form a conduction band with substantial pairing of spins. There is however, a weak electronic spin magnetization whose spin resonance can be studied. In sodium chlorine, however, the sodium gives up its outermost electron to complete the unfilled p -shell of the chlorides, resulting in a zero spin magnetization and no electron spin resonance. Covalently bonded compounds can however, show spin resonance.

In any physical investigation one invariably applies a controllable perturbing source. The behaviour of the system under such a perturbation furnishes some insight into the nature of
the system. To gain an insight into the magnitude of the required field we recall that in the hydrogen atom the field experienced by an electron due to the presence of the nucleus is of the order of $10^5$ gauss. We must therefore have a field of this magnitude in order to gain any information from the electronic system. It is to be recalled that it is this $10^5$ gauss field which physically provides a meaningful axis about which the electron spin moment takes its quantized values.

The difficulty experienced by Gorter was the fact that only low energy yields are involved. For the $x$-band, for example, at the frequency of 9254 MHz the energy involved is:

$$\Delta E = h\gamma = 67 \times 10^{-18} \text{ergs},$$

while $kT$ for one degree is $1.38 \times 10^{-16} \text{ergs}$.

This small energy can easily be swamped by noise. It is to improve the signal to noise ratio that the present day spectrometer was introduced. It not only affords a high signal to noise ratio, but also affords a high amplification.

B. Principles of ESR

When an isolated paramagnetic ion finds itself in an externally applied magnetic field $H$, its angular momentum vector precesses about $H$ with an angular velocity $\omega$ given by

$$\omega = g(e\hbar /2mc)H = gH\beta$$

(1)

where $c$ is the velocity of light, $m$ the electronic mass and $g$
the spectroscopic splitting factor.

When a varying field is applied the above situation is slightly modified. If the field is in such a sense and frequency that it is in synchronism with the ion's angular momentum vector, a constant couple then acts on the magnetization vector causing it to turn over thereby reversing its projection on \( \vec{H} \).

In practice, a linearly polarized oscillating field is used. However, this is equivalent to two rotating fields as follows: any linearly polarized oscillating field

\[
H_x = H_0 \cos \omega t
\]
can be resolved into two circularly polarized fields as follows:

\[
H_x = \frac{1}{2} H_0 \cos \omega t
\]
\[
H_y = \frac{1}{2} H_0 \sin \omega t
\]
and

\[
H_x = \frac{1}{2} H_0 \cos \omega t
\]
\[
H_y = -\frac{1}{2} H_0 \sin \omega t
\]

These two circularly oppositely directed polarized vibrations combine to give a linear motion along the diameter joining the points where the rotating radius vectors cross. The counter-rotating component of the magnetic field has no effect on the average and can be neglected.

When the reversal of the projection takes place we say that the ion has absorbed energy from the radiation field. This reversal is not continuous but quantized according to quantum mechanics.
The energy of a spin in a magnetic field is given by $Mg\beta H$ where $M$ is the projection of the angular momentum $L$ on the quantization axis and can take the values $(-L, -L + 1, \ldots, L - 1, L)$. Transitions between adjacent levels are induced by the rotating field. Such transitions are governed by the selection rule $\Delta M = \pm 1$. The resonance condition is thus

$$\hbar\nu = g\mu_B H$$

(2)

In a system of many ions we know that, provided that there exists thermal equilibrium with the surroundings, the state of lower energy is more populous. Since however, there is an equal probability between up and down transitions, the net result of application of the resonance radiation is a gain of energy from the radiation field and a shift towards equal population of levels. It is this resonance absorption that interests us. It can be detected by the loss of energy from the radiation field. This loss is measured by observing the damping of the tuned circuit in which the paramagnetic ion is placed.

As described in the next section, the energy levels of an ion in a system of interacting ions will be modified by the interactions, so that equation (2) is no longer valid.
CHAPTER II

THEORY

A. General Hamiltonian.

The general Hamiltonian contains terms describing the various effects experienced by an ion situated in a crystal. These effects are:

1. Electrostatic field of the crystal at the site of the ion \( V_X \).

2. Coulomb interaction of the electrons with the nucleus and with the neighbouring electrons \( V_G \).

3. Spin orbit coupling \( V_{LS} \).

4. Spin spin coupling between electrons \( V_{SS} \).

5. Hyperfine interaction with the nucleus \( V_N \).

6. Interaction with the nuclear quadrupole moment \( V_Q \).

7. Interaction of the electrons with the external magnetic field \( V_{HE} \).

8. Interaction of the nucleus with the external magnetic field \( V_{NH} \).

The combined effect results in the formula

\[
\mathcal{H} = V_X + V_C + V_{LS} + V_{SS} + V_N + V_Q + V_{HE} + V_{NH} \tag{3}
\]

The only terms which need be taken into account in this specific
case are: the electrostatic field of the crystal at the ion site, the hyperfine interaction with the nucleus and the interaction of the electrons with the external magnetic field. Hence the effective Hamiltonian is

\[ H_{\text{eff}} = V_{HE} + V_X + V_{NH} \]  

(4)

B. The Spin Hamiltonian of Mn\(^{2+}\) ion

The general form of the Hamiltonian is very complicated. This complexity was reduced by the introduction of the spin Hamiltonian by Pryce (1950) and Abragam and Pryce (1951). Their procedure has been outlined by Low (1960). The basic idea of the spin Hamiltonian is that the interactions are expressed in terms of spin operators and empirical constants.

The three terms in the effective Hamiltonian take the following forms:

1. The Zeeman Term.

The Zeeman term can be expressed as

\[ V_{HE} = (H \cdot g^t \cdot S)\beta \]  

(5)

where \( g^t \) represents the \( g \) tensor. Its components do not correspond to the Lande \( g \), since the former are experimentally defined quantities. It is always possible to find the principal axes along which the \( g \)-tensor is diagonal. For such axes we have

\[ V_{HE} = \beta (g_{xx}S_x + g_{yy}S_y + g_{zz}S_z) \]  

(6)
2. The Crystalline Field.

The crystalline field is represented by

$$V_X = \sum_{m n} A_n^m r_m n^m(\theta, \phi)$$  

(7)

The range of the summation index \( n \) can be considerably reduced. For the \( d \)-electrons all terms for which \( n \) is greater than 4 have zero matrix elements. These terms can be neglected. This is because in evaluating the elements \( \int \overline{\phi} U \psi d\Omega \), where \( \phi \) and \( \psi \) are the \( d \)-electron wave functions, we obtain the density \( \overline{\phi} \psi \) which, when expanded in spherical harmonics, does not contain terms for which \( n > 4 \). If \( U \) is a spherical harmonic with \( n \) greater than 4, the integral vanishes by the orthogonality relations of spherical harmonics. All terms for which \( n \) is odd vanish because \( \overline{\phi} \psi \) is unchanged by the substitution \( x, y, z \rightarrow -x, -y, -z \) while \( U \) reverses sign. If one then, neglects the case for which \( n = 0 \), the expansion of \( V_X \) with respect to \( n \) is \( n = 2 \), and \( n = 4 \). For a given \( n \), values of \( m \) are restricted by the symmetry properties of the crystalline field. For the present case of rhombic symmetry, only even \( m \) values need be considered. Also, \( m \leq n \).

Hence

$$V_X = r^2 A_2^0 y_2^0 + r^2 A_2^2 y_2^2 + r^4 A_4^0 y_4^0 + r^4 A_4^2 y_4^2 + r^4 A_4^4 y_4^4$$  

(8)

The \( A_j^i \) are the coefficients characteristic of the particular crystal field. \( A_4^0 \) and \( A_2^0 \) represent the axial part, \( A_2^2 \) and \( A_4^2 \)
the rhombic part, and \( A^+_{4}\) the tetragonal part of the ion site symmetry. In the spin Hamiltonian the above equation is expressed in the form of angular momentum operators \( O^M_n \) (see Orbach 1961, for example). The resulting field is

\[
V_x = 1/3(b_2^0 o^0_2 + b_2^2 o^2_2) + 1/60(b_4^0 o^0_4 + b_4^2 o^2_4 + b_4^4 o^4_4) \tag{9}
\]

where \( b^i_j \) are called the crystalline field parameters, and are constant multiples of \( A^i_j \).

3. The Hyperfine Interaction.

The hyperfine-structure term arises partly from the Fermi contact term

\[
\frac{3}{2} \varepsilon_e \varepsilon_N \beta \beta \delta (\hat{r}_e - \hat{r}_N) \cdot \hat{S} \tag{10}
\]

and partly from the ordinary dipole-dipole coupling

\[
- \varepsilon_e \varepsilon_N \beta \beta \langle r^{-3} \rangle [\hat{I} \cdot \hat{S} - 3(\hat{I} \cdot \hat{r})(\hat{S} \cdot \hat{r})] \tag{10a}
\]

where \( \varepsilon_N \) is the nuclear \( g \)-value, \( \beta_N \) is the nuclear magneton, \( \varepsilon_e \) the free electron \( g \), \( r_e \) and \( r_N \) the electron and nuclear distances. Bleaney (1967) discussed in full the character of the parameter \( \langle r^{-3} \rangle \).

It would appear that the introduction of the contact term is unnecessary for the divalent manganese ion. Here the \( 3d^5 \) configuration leading to the spectroscopic state \( ^6S \) is a superposition of \( d \) orbitals which vanish at the nucleus. The delta function
therefore is expected to pick out a vanishingly small coefficient for \( \hat{I}_z \hat{S} \). However it is discovered experimentally that manganese ion shows an essentially isotropic hyperfine coupling. This is now interpreted as due to a configuration interaction which admixes to \( 3s^2 3d^5 \) some \( 3s 3d^4 4s \).

Equations (10) and (10a) can be combined to give an expression of the form \( \hat{S} \cdot A \hat{I} \), where \( A \) is a symmetric tensor of the second rank. In the principal axes system this operator due to the hyperfine interaction then takes the form

\[
\mathcal{H}_C = A_{xx} S_x I_x + A_{yy} S_y I_y + A_{zz} S_z I_z
\]

(11)

The spin Hamiltonian is now given by

\[
\mathcal{H} = \beta (g_x H S_x + g_y H S_y + g_z H S_z) + \frac{1}{3}(b_2^o 0_2^o + b_2^2 0_2^2)
+ \frac{1}{60}(b_4^o 0_4^o + b_4^2 0_4^2 + b_4^4 0_4^4)
+ A_{xx} S_x I_x + A_{yy} S_y I_y + A_{zz} S_z I_z
\]

(12)

4. Transformation of the Spin Hamiltonian.

The eigenvalues of the spin Hamiltonian are generally found by applying perturbation theory. In the application of perturbation theory, the Zeeman energy is regarded as being large in comparison with the other terms. The spectral axes are chosen so as to make the \( g \)-tensor diagonal. In order to make the Zeeman energy diagonal a transformation is carried out. If the direction
of constant magnetic field $\mathbf{H}$ with respect to the crystal field axes is $(\theta, \phi)$; then due to the anisotropy of the spectroscopic splitting factor $g^t$ the Zeeman energy will be diagonal in a coordinate system rotated relative to the initial system through angles $\beta, \alpha$. These angles are shown in Figure 1, and they are related by:

\begin{align*}
\cos \beta &= \left( \frac{g^t}{\epsilon} \right) \cos \theta \\
\sin \beta &= \left( \frac{g^t}{\epsilon} \right) \sin \theta \\
\cos \alpha &= \left( \frac{g^t}{\epsilon} \right) \cos \phi \\
\sin \alpha &= \left( \frac{g^t}{\epsilon} \right) \sin \phi
\end{align*}

\begin{align*}
ge^2 &= e^2 \cos^2 \theta + e^2 \sin^2 \theta \\
e^2 &= e^2 \cos^2 \phi + e^2 \sin^2 \phi
\end{align*}

(13)

The fine structure terms can then be transformed for the rotation through $\beta, \alpha$. The transformation is carried out using the results of Baker and Williams (1961). Taking into account the transformation of the hyperfine interaction operators, Vinokurov (1964), the Hamiltonian in the new coordinate system takes the form:

$$
\mathcal{H} = e^2 H_{S_z} + \frac{1}{3} \sum_{n=0}^{2} a_n^2 \hat{c}_n^2 + \frac{1}{60} \sum_{n=0}^{4} a_n^4 \hat{c}_4^n
$$

$$
+ P S_z I_z + Q S_x I_x + R S_y I_y
$$

(14)

The above equation is valid for $H$ parallel to any spectral axis. The expressions for $a_j^i$ and $P, Q, R$ when $H$ is parallel to the spectral axes are given in Table I.
<table>
<thead>
<tr>
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<th>$H_z$</th>
<th>$H_x$</th>
<th>$H_y$</th>
</tr>
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<tr>
<td>$a_2^o$</td>
<td>$b_2^o$</td>
<td>$1/2(b_2^o - b_2^2)$</td>
<td>$1/2(b_2^o + b_2^2)$</td>
</tr>
<tr>
<td>$a_2^2$</td>
<td>$b_2^2$</td>
<td>$1/2(3b_2^o + b_2^2)$</td>
<td>$1/2(3b_2^o - b_2^2)$</td>
</tr>
<tr>
<td>$a_4^o$</td>
<td>$b_4^o$</td>
<td>$1/8(3b_4^o - b_4^2 + b_4^4)$</td>
<td>$1/8(3b_4^o + b_4^2 + b_4^4)$</td>
</tr>
<tr>
<td>$a_4^2$</td>
<td>$b_4^2$</td>
<td>$-1/2(5b_4^o - b_4^2 - b_4^4)$</td>
<td>$-1/2(5b_4^o + b_4^2 - b_4^4)$</td>
</tr>
<tr>
<td>$a_4^4$</td>
<td>$b_4^4$</td>
<td>$1/8(35b_4^o + 7b_4^2 + b_4^4)$</td>
<td>$1/8(35b_4^o - 7b_4^2 + b_4^4)$</td>
</tr>
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P  A  B  C
Q  B  A  A
R  C  C  B
FIG 1 ORIENTATION OF $\hat{H}$ AND SPIN QUANTIZATION AXIS
CHAPTER III

CRYSTALLOGRAPHY

A. General Data, Structure and Space Group

The cordierite crystal is one of the orthorhombic crystal systems with an additional lattice point on the C-face. It belongs to the space group Cccm (D_{2h}^{20}), represented in Figure 2. The general structure has been determined by Bystrom (1941). The dimensions are a = 17.06Å, b = 9.69Å, c = 9.37Å. The volume of the unit cell, which contains the formula (Al,Fe)_{2} (Mg, Fe, Mn)_{2} (Si, Al) O_{4} 0·0·1H_{2}O four times is 1549Å^{3}, with a measured density of 2.60 gm/cm^{3}.

Cordierite has a pseudo-hexagonal structure a = b√3 and is almost identical with beryl. Of the 24 tetrahedral sites in the sixfold rings of each unit cell, only four are occupied by Al and the remainder by Si (Bragg 1965). The four are made up of three sets of eight equivalent positions. To accord with symmetry the four Al atoms would have to be randomly distributed over all the 24 sites. The incooperation of water in the cordierite structure has been established but there is some uncertainty as to its location. It has been tentatively suggested (Smith 1962) that the water molecules may be attached to the walls of the large cavities in the channels enclosed by the sixfold rings, or occur partly as hydroxyl.

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FIG. 2 SYMMETRY OF Cccn
The symbol on the right hand corner denotes a reflection plane parallel to the plane of the paper at level $z = 1/4$; ---- is the glide plane seen edge on along the translation component; --- is the diagonal glide plane seen edge on; horizontal 2-fold screw axes; is the horizontal 2-fold axes; and 2-fold rotation axis normal to the reflection plane.
groups in the silicate framework. Figure 3 shows the crystal
structure.

B. Atomic Positions

The notation 4(b), 8(g) etc. refers to equipoints. An equipoint is a collection of points related to one point by the
symmetry operations of the space group. The number of points per
unit cell in an equipoint is called its rank. The numeral represents
the rank of the equipoint while the letters distinguish
several equipoints of the space group and in general indicate the
number of degrees of freedom, i.e. the number of variable coordinates.

With the origin at centre (2/m or com) the coordinates of
the equipoints are:

\[
(0,0,0; \frac{1}{2}, \frac{1}{2}, 0) + \]

\[
\begin{array}{llll}
16(m) & x,y,z; & \bar{x},\bar{y},z; & \bar{x},y,\frac{1}{2} - z; \\
 & x,\bar{y},\frac{1}{2} + z; & \bar{x},y,\bar{z}; & x,y,\bar{z}; \\
 & x,\bar{y},\frac{1}{2} + z; & \bar{x},y,\frac{1}{2} + z & 16 3 \\
8(l) & x,y,0; & \bar{x},\bar{y},0; & \bar{x},y,\frac{1}{2}; \\
 & x,\bar{y},\frac{1}{2} & \bar{x},y,0; & \bar{x},y,\frac{1}{2} & 8 2 \\
8(k) & \frac{1}{4}, \frac{1}{4}, z; & \frac{1}{4}, \frac{1}{4}, \bar{z} & \frac{1}{4}, \frac{3}{4}, \frac{1}{2} + z \\
 & \frac{1}{4}, \frac{3}{4}, \frac{1}{2} - z & \bar{x},0,1 & \bar{x},0,\frac{3}{2} & 8 1 \\
8(g) & x,0,\frac{1}{4}; & \bar{x},0,\frac{1}{4}; & \bar{x},0,\frac{3}{2} & \\
 & x,0,\frac{3}{4} & & 8 1 \\
\end{array}
\]
Fig. 3 Crystal structure projected unto (001) plane

The figures indicate the height of the atoms in percent of c. The aluminum and magnesium atoms are shown joined to their nearest oxygen neighbors.
where \( x, y, z \) are in the units of \( a, b, c \) respectively.

The atomic positions are

\[ \begin{align*}
4\text{Al}_I & \text{ in } 4(b) : \pm (0, \frac{1}{2}, \frac{3}{4}) \\
8\text{Al}_{II} & \text{ in } 8(k) : \pm (\frac{1}{4}, \frac{1}{4}, z; \frac{1}{4}, \frac{3}{4}, \frac{1}{2} + z) \\
8\text{Mg} & \text{ in } 8(g) : - (x, 0, \frac{1}{4}; \bar{x}, 0, \frac{1}{4}) \\
8(\text{Si,Al})_I & ; 8(\text{Si,Al})_{II} ; 8(\text{Si,Al})_{III} ; 8 \text{ O}_I , 8 \text{ O}_{II} \text{ and } 8 \text{ O}_{III} \\
& \text{ in } 8(l) : - (x, y, 0; x, \bar{y}, \frac{1}{4}) \\
16 \text{ O}_{IV} , 16 \text{ O}_{V} , 16 \text{ O}_{VI} \text{ in } 16(m) : - (x, y, z; x, y, \bar{z}; x, \bar{y}, \\
\frac{1}{2} + z; x, \bar{y}, \frac{1}{2} - z) \\
\end{align*} \]

with the following values for \( x, y, z \)

\[ \begin{array}{cccccc}
\text{Al}_{II} & \text{Mg} & \text{Si}_I & \text{Si}_{II} & \text{Si}_{III} \\
x & - & 0.333 & 0.190 & 0.126 & 0.062 \\
y & - & - & 0.063 & -0.255 & 0.316 \\
z & 0.260 & - & - & - & - \\
\end{array} \]
The interatomic distances in Å are

\[
\begin{align*}
\text{Al}_I & \quad 4 \ 0_v & 1.75 \\
\text{Al}_{\text{II}} & \quad 2 \ 0_{\text{VI}} & 1.81 \\
\text{Al}_{\text{III}} & \quad 2 \ 0_{\text{IV}} & 1.82 \\
\text{Mg} & \quad 2 \ 0_{\text{VI}} & 2.02 \\
\text{Mg} & \quad 2 \ 0_{\text{IV}} & 2.04 \\
\text{Mg} & \quad 2 \ 0_v & 2.09 \\
\text{Si}_I & \quad 0_{\text{III}} & 1.63 \\
\text{Si}_I & \quad 0_{\text{II}} & 1.64 \\
\text{Si}_I & \quad 0_{\text{IV}} & 1.66 \\
\text{Si}_{\text{II}} & \quad 0_1 & 1.63 \\
\text{Si}_{\text{II}} & \quad 0_{\text{III}} & 1.64 \\
\text{Si}_{\text{II}} & \quad 2 \ 0_{\text{VI}} & 1.67 \\
\text{Si}_{\text{III}} & \quad 0_1 & 1.63 \\
\text{Si}_{\text{III}} & \quad 0_{\text{II}} & 1.64 \\
\text{Si}_{\text{III}} & \quad 2 \ 0_v & 1.65
\end{align*}
\]

The shortest O—O distance is 2.50 Å.
Fig. 4 Magnesium-Oxygen angular relations

- Mg above the plane of paper
- O₂ below the plane of paper

Mg-O₂ distance 2.05 Å
C. Site of Mn$^{2+}$

The angular relation between oxygens and the magnesium atom is shown as a projection on the ac-plane in figure 4.

Magnesium is situated in a strongly distorted octahedron. The distortion is along the three-fold axis, which corresponds with the c-axis of the crystal. The distortion can be visualized as a compression along the c-axis of the crystal. This distortion slightly disrupts the three-fold symmetry.

From the general formula of cordierite one would expect that Fe$^{2+}$ or Mn$^{2+}$ can substitutionally replace Mg, while Fe$^{3+}$ can do the same for Al. In fact the latter has been studied by Hedgecock and Chakravartty (1966). Because a single spectrum was observed we concluded that there was only one manganese site.

The spectral axes coincide, within experimental error, with the crystallographic axes, with the z-axis lying along the c-axis. The spectrum shows only a small deviation from axial symmetry about the c-axis. These facts are consistent with the assumption that manganese is located at the magnesium site.
CHAPTER IV

APPARATUS

The ESR spectrometer used to study resonance of impurity manganese in cordierite was of the straight-detection type. The block diagram of the spectrometer is given in Figure 5. It employs the Varian 203B/6975 reflex klystron with a power rating of 50 milliwatts and a tunable frequency range of 8.4 to 9.5 GHz.

The klystron microwave frequency was stabilized to the cavity resonant frequency by the Pound type stabilizer which operates as follows: A 450 kHz signal was used to slightly frequency modulate the klystron. The 450 kHz signal reflected from the cavity was detected by the AFC crystal detector, amplified and applied to the phase sensitive detector, where it was compared with the original modulation signal. The resultant dc error voltage was applied to the klystron reflector. This pulls the microwave frequency to coincide with the cavity resonant frequency.

The cavity employed in the spectrometer was a rectangular TE_{102} type. The cavity houses the specimen mounted on a nylon pin and rotated by a worm and pinion wheel mechanism. This rotating
mechanism is shown in Figure 6. 100 KHz modulation of the magnetic field was obtained on a single loop within the cavity.

Some of the other wave guide components are mentioned below with their functions. The isolator is a two-terminal pair microwave ferrite device which makes use of the Faraday effect to permit transmission of microwaves in one direction and prevents their transmission in the opposite direction. The microwaves pass through a magnetised ferrite material. This results in the Faraday rotation of the plane of polarization of the microwaves. The Ferranti three port circulator model 211XCD was used. The circulator has the property of transmitting power from one terminal to the other in sequence. With the klystron placed in port one, the resonant cavity in port two and detector in port three, the circulator, which also contains ferrite material, allows the klystron power to go directly to the cavity and the signal reflected at resonance to go directly to the detector. No power is transferred directly from klystron to detector. The cavity arm can be matched to the klystron arm by means of a slide-screw tuner. An ESR absorption in the cavity then causes a mismatch, so that power is reflected from the cavity into the detector arm. In practice the cavity is slightly mismatched in order to allow sufficient power to bias the detector crystal.

The external magnetic field was provided by a Newport water cooled magnet. In the studies at room temperature, conical pole tips $\frac{5}{2}$" face diameter were used. At liquid nitrogen
FIG. 6 ROTATING MECHANISM FOR THE CRYSTAL IN THE $^{102}$ CAVITY
temperature plane pole tips or 7" face diameter were employed in order to accommodate the glass Dewar.

The magnetic resonance signal from the cavity was detected by the resonance crystal detector and applied to the P.A.R. lock in amplifier, from whose reference voltage the 100 KHz modulation was obtained. The output obtained was proportional to the derivative of the microwave absorption. This magnetic resonance was displayed as the derivative of the absorption against the magnetic field either on an oscilloscope or on a chart-recorder.

Proton magnetic resonance equipment was used to measure the resonant fields.
CHAPTER V

EXPERIMENTAL PROCEDURE

Experiments were carried out at two temperatures - room temperature and liquid nitrogen temperature. The experimental procedure was the same for the two temperatures.

A. Location of the Spectral Axes

The usual procedure for spectrometer adjustment was carried out.

The location of the spectral axes has in principle been outlined by Manoogian et al (1955). The above implies that one would expect, for the type of spectrum under consideration, the resonances to be most widely separated along the $z$-axis. Once this axis has been found, the $x$-axis is chosen as that along which the resonances are least separated.

The general outline in location of the axes is as follows: By rotating the crystal and the magnet, a fairly strong line is selected for observation on the oscilloscope. The movement of the
Fig. 7 (a) Calibration of Mullif net with angles $\theta$ and $\phi$. Z-axis and xy-plane are shown. (b) The three spectral axes and xy-,yz-,zx- planes are shown.
line with the alternate rotation of the crystal and magnet, will show that it moves either to the direction of the high field or to the direction of low field. The dual rotation is chosen so that the movement is towards the high field for lines on the high field side, and towards low field for lines on the low side. The other lines on both sides of the DPPH marker are similarly followed. The magnet and crystal angles at which the above condition obtained are taken as the coordinate of the $z$-axis.

The other two axes were located using the Wulff net. A typical calibration of the net is shown in Figure 7. We used negative and positive angles to coincide with the graduation on the magnet. Here $\phi$ is the angle in the horizontal plane between the magnetic field direction and the crystal rotation axis. It is obtained from the magnet scale. $\theta$ read from the crystal rotation scale is the angle between the vertical (the axis of the magnet rotation) and crystal edge.

The use of Wulff net is as follows: A transparent sheet is placed over the Wulff net and the $z$-axis is marked. The tracing paper is rotated to bring the $z$-axis on the $0-180^\circ$ line, and counting out $90^\circ$ from this axis, a curve representing the $xy$-plane is drawn along a great circle. The tracing paper is then brought back to its original position. We now know that the other two axes will lie on the $xy$-plane. We now know the pairs of coordinates $(\phi, \theta)$ which we can investigate. The spectrum is examined
at points along this plane and the x-axis is chosen as the point for which the spread of the spectrum is a minimum. The location of the x-axis, leads, with the located z-axis and the fact that the y-axis must be 90° away from x-axis, to location of y. The located x-axis and z-axis are brought to the same great circle and the xy-plane drawn. The z-axis is placed on the 0–180° and from x-axis a point is marked along the xy-plane 90° away. This point is the y-axis.

It is difficult to follow line movements along the xy-plane since according to Manoogian et al. (1955), near the y-axis the lines exhibit inflection—maximum spread in xy-plane and minimum spread in xy-plane.

The final position of the x- and y-axes are checked by taking recordings about the axes so found and comparing the spread of the spectrum.

If after locating the z-axis and the x-axis it was found that the y-axis is located at large magnet angles where the intensity is very low, the crystal was remounted making judicious use of the axes so far found. Several remounts were made before it was possible to locate the axes along relatively small magnet angles where the line intensities were relatively high. Recordings of the spectrum were made along each axis.
B. The Measurement of Resonant Fields

The resonant frequencies were measured by superimposing an NMR signal on the ESR signal on the oscilloscope. The frequencies were converted into fields by using the relation that a proton frequency of 4.25759 MHz corresponds to 1 kilogauss field.

C. Low Temperature Work

A glass Dewar was used. The cavity was purged with nitrogen. The system was evacuated for a short time before liquid nitrogen was introduced. Since the system was not vacuum tight, pumping was continuous.
CHAPTER VI
ANALYSIS OF EXPERIMENTAL RESULTS

The spectra when the magnetic field was parallel to the x, y, and z axes respectively were interpreted in terms of the following formulae derivable from eigenvalues of the Hamiltonian of equation 14 (Vinokurov 1964).

\[
H (\pm 5/2, m \leftrightarrow \pm 3/2, m) = H_0 \mp 4a_2^0 \mp 4a_4^0 + m P \mp (2QRm)/H_o
- (a_4^2)^2/(20H_o) - (a_2^2 a_4^2)/H_o + 4(a_2^2)^2/9H_o
- (q^2 + R^2) [I(I + 1) - m^2] / 4H_o \tag{15}
\]

\[
H (\pm 3/2, m \leftrightarrow \pm 1/2, m) = H_0 \mp 2a_2^0 \pm 5a_4^0 - m P \mp QRm/H_o
- 5(a_2^2)^2/9H_o - 9(a_4^2)^2/80H_o - (a_2^2)^2/20H_o
- (a_2^2 a_4^2)/2H_o
- (q^2 + R^2) [I(I + 1) - m^2] / 4H_o \tag{16}
\]

\[
H (-1/2, m \leftrightarrow -1/2, m) = H_0 - m P - 8(a_2^2)^2/9H_o - (a_2^2)^2/10H_o 2a_2 a_4^2/H_o
- (q^2 + R^2) [I(I + 1) - m^2] / 4H_o \tag{17}
\]
TABLE II

RESONANT FIELDS FOR T=300°K. VALUES IN KILOGAUSS.

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<thead>
<tr>
<th>Transition</th>
<th>5/2 → 3/2</th>
<th>3/2 → 5/2</th>
<th>1/2 → 3/2</th>
<th>3/2 → 1/2</th>
<th>3/2 → 3/2</th>
<th>5/2 → 5/2</th>
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<td></td>
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<td>1.5087</td>
<td>1.5987</td>
<td>1.6830</td>
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<tr>
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<table>
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<th>3/2 → 5/2</th>
<th>1/2 → 3/2</th>
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<th>3/2 → 5/2</th>
<th>1/2 → 3/2</th>
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<th>5/2 → 5/2</th>
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<td>x</td>
<td>3.4232*</td>
<td>3.5140*</td>
<td>3.5917*</td>
<td>3.6767*</td>
<td>3.7660*</td>
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<td>3.5798*</td>
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<th>3/2 → 5/2</th>
<th>1/2 → 3/2</th>
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<td>4.8789</td>
<td>4.9787</td>
<td>5.0749</td>
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* Not used in numerical analysis
<table>
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<th>$\frac{3}{2} \rightarrow \frac{3}{2}$</th>
<th>$\frac{1}{2} \rightarrow \frac{1}{2}$</th>
<th>$-\frac{1}{2} \rightarrow -\frac{1}{2}$</th>
<th>$\frac{3}{2} \rightarrow \frac{3}{2}$</th>
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</tr>
<tr>
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<tr>
<td>$H_{</td>
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<td>x}$</td>
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<td>3.9941</td>
<td>4.0782</td>
<td>4.1641</td>
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</table>
where the parameters $a_j^i$, $Q$, $R$, and $P$ are given in Table I. The measured resonant fields with the magnetic field along the three spectral axes are shown in Tables II and III. The traces of the spectra at the X-band are shown in Figures 9 and 10. Figure 9 was obtained at room temperature while Figure 10 was obtained at liquid nitrogen temperature.

A. Preliminary Estimation of Parameters

From the measurement along the z-axis it was possible to estimate the values of $b_2^o$ and $b_4^o$. The full thirty lines are visible along the z-axis at room temperature. Consider such set of lines:

<table>
<thead>
<tr>
<th>Group</th>
<th>1</th>
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<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>d</td>
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<td></td>
<td>f</td>
<td>a</td>
<td>f</td>
<td>a</td>
<td>f</td>
</tr>
</tbody>
</table>

On neglecting the second order term $BCm/H_0$, we can derive the following equations from the resonant fields.

\[
\begin{align*}
H_{5f} - H_{1f} &= 8a_2^o + 8a_4^o = d \\
H_{4f} - H_{2f} &= 4a_2^o - 10a_4^o = d' \\
H_{5a} - H_{1a} &= 8a_2^o + 8a_4^o = d'' \\
H_{4a} - H_{2a} &= 4a_2^o - 10a_4^o = d'''
\end{align*}
\]

Hence

\[
8a_2^o + 8a_4^o = \frac{1}{2} (d + d''')
\]

\[
4a_2^o - 10a_4^o = \frac{1}{2} (d' + d''')
\]

$a_j^i$ are given in Table I. $b_2^o$ and $b_4^o$ were obtained from the spectrum along the z-axis. From the incomplete results along the other two
Figure 8: Trace of the spectra when spectral axes at room temperature. The arrow indicates the direction of increasing magnetic field.
FIG. 9 TRACE OF THE SPECTRA WHEN $H_m$ SPECTRAL AXES AT LIQUID NITROGEN TEMPERATURE

The arrow indicates the direction of increasing Magnetic Field.
The quantities $b_2^2 + (5/8)b_4^2$ were calculated, and an estimate of $b_4^2$ was made. The latter is rather uncertain since the previously obtained values of $b_2^2$ and $b_4^0$ had to be used. Independent evaluation of $b_2^2$ and $b_4^2$ is only possible if second order terms are taken into account.

The sign of $A$ was determined by examination of the separation of the hyperfine lines along the $z$-axis. An increase in the separation within the hyperfine groups in the direction of increasing magnetic field indicates that the sign of $A$ is negative. This is evident from the equations for the resonant fields. The hyperfine constants $B$ and $C$ have the same sign as $A$.

B. Detailed Calculation by Computer.

The basic computation procedure is as follows: The measured resonant fields or centres of gravity are compared with those calculated from the initial parameters. The differences are then used to calculate corrections to these parameters. This process is repeated until no further significant change in the parameters occurs.

It is not practical to use all the individual resonant fields in such a process, since the computer time involved in solving up to 90 equations in 11 unknowns is prohibitive. Furthermore, with so many equations, the validity of the procedure is questionable, and problems might arise with accumulation of
Figure 10. Flow diagram for computer computation.
errors.

An attempt was made to fit the spectrum for each axis separately, with the intention of combining the results for each. No meaningful results were, however, obtained.

It was decided to use the centres of gravity in the detailed computation. The calculated centres of gravity (CGC) are obtained from Vinokurov's equations using the preliminary estimates of the parameters \( p_{est} \). The experimental centres of gravity (CGX) are regarded as functions of the yet unknown "true" parameters \( p_{true} \), which are assumed to be related to \( p_{est} \) by

\[
P_{true} = p_{est} + \Delta
\]

The CGX can then be expressed in the form

\[
CGX = CGC + \sum \frac{\partial CG}{\partial P_i} \Delta_i
\]

so that the difference is

\[
W = CGX - CGC = \sum \frac{\partial CG}{\partial P_i} \Delta_i
\]

This can be expressed in the abbreviated form

\[
\hat{W} = \hat{D} \hat{\Delta}
\]

If there are \( NC \) measured centres of gravity and \( N \) parameters, \( W \) is a vector of \( NC \) components, \( D \) is a \( NC \times N \) matrix and \( \Delta \) is a vector of \( N \) components. This system of equations is now reduced by multiplying both sides of equation (22) by the transpose of \( \hat{D} \).

Then

\[
\hat{D}^T \hat{W} = \hat{D}^T \hat{D} \hat{\Delta}
\]

which gives \( N \) equations in \( N \) unknowns \( \Delta_i \). This reduction ensures that
**TABLE IV**

**EXPRESSIONS FOR h AND Hₙ FOR INCOMPLETE Dᵢ's**

<table>
<thead>
<tr>
<th>Missing Dᵢ</th>
<th>Expression for h</th>
<th>Expression for Hₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₁</td>
<td>$$(D₂ - D₃)/2$$</td>
<td>$$(17D₂ - 13D₃)/2$$</td>
</tr>
<tr>
<td>D₂</td>
<td>$$(D₁ - D₃)/6$$</td>
<td>$$(17D₁ - 5D₂)/12$$</td>
</tr>
<tr>
<td>D₃</td>
<td>$$(D₁ - D₂)/4$$</td>
<td>$$(13D₁ - 5D₂)/8$$</td>
</tr>
</tbody>
</table>
the solution vector $\Delta$ is such that the corrected parameters give a least square fit to the original $\bar{W}$. This procedure can be repeated as often as required.

In the computation sketched in Figure 10 the parameters $b_{ij}^1$ and $c_{ij}^1$ were calculated. The hyperfine constants were obtained directly from the resonant fields. The computation was carried out using the IBM 1620 machine.

As a further check the centres of gravity were treated as lines in the spectrum of the isoelectric trivalent iron ion. They were then used in a similar calculation using a programme developed by J. R. Thyer. In order to obtain meaningful results it was necessary to make a correction for the second order term in the manganese centres of gravity. The results obtained from this were for checking purposes only, since there is a large uncertainty in the second order correction.

The corrections were made as follows:

The average of the pair of lines in a hyperfine group can be represented by $\frac{1}{2}(H_1 + H_6)$, $\frac{1}{2}(H_2 + H_5)$, $\frac{1}{2}(H_3 + H_4)$, $H_i$ are the resonant fields. If $D_i$ ($i = 1, 2, 3$) be the difference between the centres of gravity in the absence of hyperfine contribution ($H_n$) and the hyperfine term $h = (B^2 + C^2)/4H_o$, then we have:

$$\frac{1}{2}(H_1 + H_6) = H_n - (5/2)h = D_1$$

$$\frac{1}{2}(H_2 + H_5) = H_n - (13/2)h = D_2$$

(24)
### TABLE V

PARAMETERS CALCULATED WITH THE CORRECTED CENTRE OF GRAVITY APPLIED TO THE IRON PROGRAMME

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$300^\circ K$</th>
<th>$77^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_2^0$</td>
<td>421.1</td>
<td>439.6</td>
</tr>
<tr>
<td>$b_2^2$</td>
<td>42.6</td>
<td>1.4</td>
</tr>
<tr>
<td>$b_4^0$</td>
<td>-4.8</td>
<td>-2.8</td>
</tr>
<tr>
<td>$b_4^2$</td>
<td>2.1</td>
<td>17.9</td>
</tr>
<tr>
<td>$b_4^4$</td>
<td>-28.8</td>
<td>24.0</td>
</tr>
<tr>
<td>$\varepsilon_x$</td>
<td>1.8198</td>
<td>2.0057</td>
</tr>
<tr>
<td>$\varepsilon_y$</td>
<td>1.9970</td>
<td>1.9951</td>
</tr>
<tr>
<td>$\varepsilon_z$</td>
<td>1.9962</td>
<td>1.9971</td>
</tr>
</tbody>
</table>

The $b_j^i$ are in units of gauss.
\[ \frac{1}{2}(H_3 + H_4) = H_n - (17/2)h = D_3 \]

Hence
\[ h = \frac{5D_1 - D_2 - 4D_3}{28} \]
\[ H_n = \frac{11D_1 + D_2 - 4D_3}{8} \]

The expressions for \( h \) and \( H_n \) when all the \( D_i \)'s are not measurable are given in Table IV. The result of the parameters from the iron programme are shown in Table V.

C. Errors.

The greatest source of error was due to the line width which is of the order of hyperfine separation. The line width was unaffected by temperature. This resulted in relatively large uncertainties in the measurement of the lines especially in the weak outer groups. Uncertainty in each measurement was taken to be 5 gauss and on this basis we estimated the experimental errors entered in Table VI. In addition all the parameters were used as calculated to determine the effect they have individually on the rms and maximum error when varied over and above a preset value. The results, also tabulated in Table VI indicate the range of parameter values for which no significant change in the fit occurred.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>300°C</th>
<th>77°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fit (±)</td>
<td>Experimental error (±)</td>
</tr>
<tr>
<td>( b_2^0 )</td>
<td>422.3</td>
<td>0.5</td>
</tr>
<tr>
<td>( b_2^2 )</td>
<td>26.5</td>
<td>2</td>
</tr>
<tr>
<td>( b_4^0 )</td>
<td>-4.3</td>
<td>0.3</td>
</tr>
<tr>
<td>( b_4^2 )</td>
<td>-12.9</td>
<td>3</td>
</tr>
<tr>
<td>( b_4^4 )</td>
<td>-23.3</td>
<td>0.3</td>
</tr>
<tr>
<td>( e_x )</td>
<td>1.9969</td>
<td>0.0006</td>
</tr>
<tr>
<td>( e_y )</td>
<td>1.9971</td>
<td>0.0005</td>
</tr>
<tr>
<td>( e_z )</td>
<td>1.9969</td>
<td>0.001</td>
</tr>
<tr>
<td>A</td>
<td>-89.9 *</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>-88.6 *</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>-89.4 *</td>
<td>5</td>
</tr>
</tbody>
</table>

\* These were not computed but calculated directly from the resonant fields. The \( b_j^j \) and the hyperfine constants are in gauss.
CHAPTER VII

CONCLUSION

In this study it was possible to obtain and interpret the ESR spectrum of Mn$^{2+}$ in cordierite. The spectrum consisted of the usual five groups of six lines which were only completely resolved for the magnetic field parallel to the $z$-axis of the spectrum. The lines were very broad, of the order of the hyperfine separation. The width of these lines were not affected by temperature. The spectrum was interpreted as arising from manganese atoms located at the magnesium site in the crystal.

The constants of the spin Hamiltonian were found. These are shown below in gauss for the $b_{ij}^0$ and the hyperfine constants. The results of liquid nitrogen temperature measurements are in brackets. $b_{2}^0 = 422.3 \, (432.1)$, $b_{2}^2 = 26.5 \, (18.4)$, $b_{4}^0 = -4.3 \, (-4.8)$, $b_{4}^2 = -12.9 \, (3.2)$, $b_{4}^4 = -23.3 \, (-14.5)$, $A = -89.9 \, (-89.2)$, $B = -88.6 \, (-93.5)$, $C = -89.4 \, (-92.0)$, $\varepsilon_x = 1.9981 \, (2.0019)$, $\varepsilon_y = 1.9971 \, (1.9977)$, $\varepsilon_z = 1.9969 \, (1.9962)$
BIBLIOGRAPHY


VITA AUCTORIS

The author was born in 1936 in Ifiteukpo Biafra (E. Nigeria). He completed his elementary school at Awkuzu, Biafra in 1947. In 1948 he taught at Ogbunike Catholic School. In 1954 he received his Cambridge Overseas' School Certificate. He received his Grade II Teachers' Certificate in 1956 and subsequently taught for a year at St. Matachy's Teacher training College, Minna, Nigeria, and at St. John's College, Kaduna, Nigeria for two years. The author in 1960 obtained the University of London Advanced Level Certificate. He received in 1966 the degree of Bachelor of Science (Special) with Hons. in Physics from the University of London, England. He is a graduate of the Institute of Physics 1966.

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