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# A STUDY OF THE EPR SPECTRUM OF ${\rm Mn}^{2^+}$ impurity in brucite

by

Robert Blaire Waite

## A Thesis

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

Windsor, Ontario

1970

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#### ABSTRACT

The temperature variation of the electron paramagnetic resonance spectrum of  $Mn^{2^+}$  impurity in the natural crystal brucite,  $Mg(OH)_2$ , was studied in the temperature range  $77^{\circ}K - 295^{\circ}K$  at K-band frequencies. The spectrum was fitted to the spin-Hamiltonian

$$\mathcal{H}_{s} = \beta \left[ g_{\parallel} \right]_{z}^{H_{z}} \left[ g_{z}^{S_{z}} + g_{\perp} \left( g_{x}^{H_{x}} \right)_{x}^{S_{x}} + g_{y}^{H_{y}} \right]$$
  
+  $\frac{1}{3} b_{2}^{\circ} o_{2}^{\circ} + \frac{1}{60} b_{4}^{\circ} o_{4}^{\circ} + \frac{1}{60} b_{4}^{\circ} o_{4}^{3}$   
+  $A S_{z} I_{z}^{I_{z}} + B(S_{x} I_{x}^{I_{z}} + S_{y} I_{y})$ 

At room temperature  $(295^{\circ}K)$  the following values were obtained for the parameters:

 $g_{\parallel} = 2.0010 \pm 0.0005 \qquad g_{\perp} = 2.0010 \pm 0.0005$  $A = -90.74 \pm 0.25 \text{ G} \qquad B = -89.69 \pm 0.25 \text{ G}$  $b_{2}^{0} = -5.85 \pm 0.50 \text{ G} \qquad b_{4}^{0} = -4.31 \pm 0.50 \text{ G}$  $b_{4}^{3} = 0 \pm 150 \text{ G}$ 

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The variation with temperature of the parameters followed similar trends as those observed by Quick<sup>9</sup> for the same impurity in the isomorphic crystal,  $Ca(OH)_2$ . Discrepancies between the parameters at X-band, as found by Pieczonka et al.<sup>17</sup>, and at K-band were found.

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#### CHAPTER I

#### INTRODUCTION AND PURPOSE OF THE EXPERIMENT

The first investigations into magnetism were carried out in 600 B.C. by the father of Greek science, Thales of Miletus. He experimented with the mineral magnetite and found it attracted ordinary iron, which itself became magnetized by touching the magnetite. Minerals which exhibit the properties of iron have since been classified as ferromagnetic. Minerals which are attracted to magnetite or other magnetic materials, but do not become permanently magnetized are called paramagnetic. Magnetism has been studied throughout history and found its first significant application in the field of navigation. The modern investigation of magnetism begins just before the turn of the century with the work of such people as Weiss, Curie, and Langevin.

Further major developments awaited the new quantum theory of the early nineteen hundreds, which was founded upon the empirical results of such works as the Stern-Gerlach, Zeeman, and the photoelectric experiments. Out of the quantum theory came speculation about dynamic phenomena which should be expected in magnetic materials and paramagnetic materials in particular. Two dynamic phenomena, which were predicted about paramagnetic materials, are paramagnetic relaxation, and resonance.

The attempts to observe paramagnetic relaxation preceded the work on paramagnetic resonance and were pursued extensively in the

- 1 -

mid nineteen thirties by predominantly scientists from the Netherlands. Two early review articles on the relaxation investigations are by Gorter<sup>1</sup> and Cooke<sup>2</sup>.

Paramagnetic resonance with which the experiment dealt, was first observed successfully by Zavoisky<sup>3</sup> in 1945. His initial experiments used a 25-meter wavelength to observe absorption as a function of magnetic field in substances whose line widths were about 50 gauss or larger. A resonance line was scarcely discernible at such low frequencies, which corresponded to a resonance 'peak' at about 4 gauss. The second series of experiments by Zavoisky<sup>4</sup> found a maximum for Cu<sup>2+</sup> ion at 47.6 gauss, using a frequency of 133 Mc sec<sup>-1</sup>.

The first work on  $Mn^{2^+}$  was completed shortly after in the United States by Cummerow and Halliday<sup>5</sup>. The results consisted of a resolved spectrum of  $Mn^{2^+}$  in 173 g. of  $MnSO_4 \cdot 4H_2^{0}$  placed in a resonant cavity excited at 2930 Mc sec<sup>-1</sup>. Then followed a period of very productive work at the Clarendon Laboratory at Oxford. The early developments in the field are chronicled in two reports by members of the Oxford group<sup>6,7</sup>.

According to Russel-Saunders coupling iron group ions with  $d^5$  configurations eg.  $M_n^{2+}$  and Fe<sup>3+</sup> and the rare earth group ions with  $f^7$  configurations, have S ground states. Any degeneracy in the ground state must be due to spin only. Bethe, in 1929, had predicted that the presence of a crystal field would remove the S-state degeneracy, and resonance studies verified this prediction. The S-state splittings can be described using a spin-Hamiltonian, which takes into consideration the crystal field interactions, hyperfine interactions, and

sometimes, superhyperfine interactions. The interactions will be discussed and the spin-Hamiltonian derived in Chapter II. To determine the amount of splitting which is due to each interaction one must determine the value of the parameter or tensor in the spin-Hamiltonian associated with that interaction.

In recent years interest has been shown both experimentally and theoretically in the temperature dependence of the parameters of the spin-Hamiltonian. Walsh et. al.<sup>8</sup>, in 1965, studied experimentally the temperature dependence of the spin-Hamiltonian parameters in cubic crystals such as MgO. The axial crystal field parameters'variation with temperature can be explained on the effect of thermal expansion on a rigid lattice model. The hyperfine parameters'variation could not be explained by a rigid model, however. It was proposed that the hyperfine parameter variations were due to lattice vibrations. Quick  $\frac{9}{7}$ , in 1969, carried out a thorough temperature study of Mn<sup>2+</sup> in a trigonal crystal field in an effort to apply the present dynamic and static models to a slightly less symmetric field than cubic.

The purpose of this experiment, which was a temperature dependence study of  $Mn^{2^+}$  in Brucite, a  $Mg(OH)_2:Mn^{2^+}$  system, was to supply additional empirical parameter measurements for a trigonal field. The hope was to provide more data to correlate with others working in temperature dependence studies, so that present models could be validified or modified in light of these new results.

#### CHAPTER II

#### THEORY

## II.1 Resonance Condition For a Free Ion

In a free ion, obeying Russel-Saunder's coupling, the total electronic angular momentum  $\underline{J}$  is given by

$$\underline{J} = \underline{L} + \underline{S} \tag{II.1}$$

The  $\underline{L}$  is the orbital electronic momentum

$$\underline{\mathbf{L}} = \sum_{\mathbf{k}} \frac{\ell}{\mathbf{k}} , \qquad (11.2)$$

and  $\underline{S}$  is the electronic spin angular momentum

$$\underline{\mathbf{S}} = \underline{\mathbf{\Sigma}} \, \underline{\mathbf{s}} \, , \qquad (11.3)$$

where  $\underline{S}_k$  and  $\underline{\ell}_k$  are summed over all electrons in the unfilled orbital of the ion.

In the presence of a magnetic field  $\underline{H}_{o}$ , quantization of the total electronic angular momentum in the direction of  $\underline{H}_{o}$  takes place. The values of the projection  $M_{J}$  that are allowed by quantum theory are:

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$$-J, -J + 1, -J + 2, - - -, J - 1, J = M_{J}$$
(II.4)

With each value of  ${\rm M}_{\rm J}$  is associated an energy given by

$$E = g \beta H M_{I}, \qquad (II.5)$$

where g is the Lande g factor given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}, \quad (II.6)$$

and  $\beta$  is the Bohr magneton given by

$$\beta = \frac{e \hbar}{4mc} . \qquad (II.7)$$

If now an alternating magnetic field of frequency v is applied at right angles to the fixed magnetic field  $\frac{H}{O}$ , magnetic dipole transitions of energy hv may be induced. Magnetic dipole transitions satisfy the selection rule

$$\Delta M_{T} = \pm 1. \tag{II.8}$$

The energy hv absorbed from the alternating magnetic field must equal the difference in energy between two levels for which  $\Delta M_J = 1$ . Hence the condition for absorption to take place is

$$h_{\gamma} = g \beta H_{a}. \tag{II.9}$$

The energy of induced emission would satisfy the same relation.

The probabilities for emission and absorption are equal, and if the two states were populated equally no net absorption would occur. Generally, the upper levels are populated less than the lower levels according to Boltzmann statistics and a net absorption of energy takes place. If sufficient power is supplied by the alternating field, the levels will be populated equally, and no more net absorption will occur. Saturation takes place.

## II.2 The General Hamiltonian

The Hamiltonian operator of a system is a quantum mechanical operator whose eigenvalues are the energies of the states of the system. To find the energy levels of an ion placed in a crystal field it is necessary to first formulate the Hamiltonian considering all possible interactions.

Abragam and Pryce<sup>10</sup> express the Hamiltonian for an iron group ion or  $Mn^{2+}$  in a crystal placed in a magnetic field as

$$\mathfrak{K} = \mathbf{v}_{F} + \mathbf{v} + \mathbf{v}_{LS} + \mathbf{v}_{SS} + \mathbf{v}_{H} + \mathbf{v}_{N} + \mathbf{v}_{Q} + \mathbf{v}_{NH}.$$
(II.10)

The terms have been arranged in decreasing order of importance.

The first term  ${\rm V}_{\rm F}$  represents the interaction associated with the free ion, considering only electrostatic interactions, and may be written as

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$$V_{F} = \sum_{i=1}^{N} \left[ \frac{P_{i}^{2}}{2m} - eV(r_{i}) \right] + \sum_{i < k}^{N} \frac{e^{2}}{r_{ik}}$$
(II.11)

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The summation is over N, the total number of electrons in the ion. eV(r,) gives the electrostatic energy due to attraction between the i<sup>th</sup> electron and the nucleus,  $\frac{\frac{P_i}{2m}}{2m}$  the linear momentum of the i<sup>th</sup> electron, and  $\frac{e^2}{r_{ik}}$  the electrostatic energy due to the repulsion between the ith and k<sup>th</sup> electron. When we consider the electrons in the unfilled 3d orbital, we find that the electrostatic interaction causes the electron levels to be grouped into states called 'terms', characterized by  $\underline{L}$  and  $\underline{S}$ .  $\underline{L}$  and  $\underline{S}$  are given in equations (II.2) and (II.3). This method of coupling electron states is known as 'L - S' or Russel-Saunders coupling. Each term is (2 J + 1) degenerate, where <u>J</u> is given by Eq. (II.1). For an ion with  $3d^5$  configuration,  $Mn^{2+}$ , there are many allowed terms including  ${}^{6}S$ ,  ${}^{4}G$ ,  ${}^{4}P$ ,  ${}^{4}D$  etc. The left superscript refers to the S-degeneracy and equals (2 S + 1). The capital letter refers to the L- value of the term, where S, P, D, F, G, --- correspond to L = 0, 1, 2, 3, 4, ---. For  $Mn^{2+}$  the lowest energy term is <sup>6</sup>S, which corresponds to one electron in each of the 3d orbitals and all spins aligned parallel, giving an  $\underline{L}$  of 0 and  $\underline{S}$ value of 5/2. The level separations of  ${\rm V}^{}_{\rm F}$  are usually of the order of  $10^5 \text{ cm}^{-1}$ .

The next term V is the electrostatic interaction with the field of the neighbouring ion. In the case of the iron group, V causes splittings of the order  $10^4$  cm<sup>-1</sup>. The term V, commonly called the crystal field term, will be discussed further in II.3.

The term  $V_{LS}$  is the spin-orbit interaction and is given

by

$$V_{LS} = \sum_{j,k}^{N} a_{jk} \pounds_{j} \cdot \underline{S}_{k} + b_{jk} \pounds_{j} \cdot \pounds_{k} + c_{jk} \underline{S}_{j} \cdot \underline{S}_{k} \quad (II.12)$$

where  $a_{jk}$ ,  $b_{jk}$ ,  $c_{jk}$  are constants. The spin-orbit interaction gives rise to splittings of the order  $10^2$  cm<sup>-1</sup>.

The term  $\rm V^{}_{SS}$  represents the magnetic dipole-dipole interaction between electrons. It is written

$$V_{SS} = \sum_{j,k} \frac{\frac{S_j \cdot S_k}{r_{jk}^2}}{r_{jk}^2} - \frac{3(\frac{r_{jk}}{s_j} \cdot \frac{S_j}{s_j})(\frac{r_{jk}}{s_k} \cdot \frac{S_k}{s_k})}{r_{jk}^5}$$
(II.13)

where the summation is over all pairs of electrons. Spin-spin interactions give rise to splittings of the order 1 cm<sup>-1</sup>.

The interaction with the external magnetic field  $\frac{H}{-0}$  is given by

$$V_{\rm H} = \sum_{\rm k} \beta \left( \frac{3}{2}_{\rm k} + 2 \underline{S}_{\rm k} \right) \cdot \underline{H}_{\rm o}$$
$$= \beta \left( \underline{L} + 2 \underline{S} \right) \cdot \underline{H}_{\rm o} \qquad (II.14)$$

These Zeeman splittings are of the order 1 cm<sup>-1</sup>.

The V term represents the magnetic interaction between unpaired electrons and the nuclear magnetic moment  $\underline{I}$ .

$$V_{N} = 2 \gamma \beta \beta_{N} \left[ \sum_{k} \left\{ \frac{\left(\frac{\ell}{k} - \underline{S}_{k}\right) \cdot \underline{I}}{k} + 3 \frac{\left(\underline{r}_{k} \cdot \underline{S}_{k}\right)\left(\underline{r}_{k} \cdot \underline{I}\right)}{r_{k}} \right\} + \frac{8\pi}{3} \delta (r_{k}) \left(\underline{S}_{k} \cdot \underline{I}\right) \right]$$
(II.15)

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Here  $\beta_N$  and  $\gamma$  refer to the nuclear magneton and the nuclear gyromagnetic ratio. The V<sub>N</sub> term is commonly called the hyperfine term and gives rise to splittings of the order  $10^{-1}$  to  $10^{-3}$  cm<sup>-1</sup>.

The term  $V_Q$  describes the electrostatic interaction with the quadrupole moment Q of the nucleus, and  $V_{\rm NH}$  the interaction of the nucleus with the external magnetic field  $\underline{\rm H}_{\rm O}$ . The last two terms cause perturbations of the energy levels of the order  $10^{-2}$  to  $10^{-3}$  cm<sup>-1</sup> and since their effect is so small will be disregarded in the following and since their effect is so small will be disregarded in the following

#### III.3 The Crystal Field

When a paramagnetic ion is placed in a crystal environment, it is now subject to a non-spherical electric potential arising from its immediate environment, and the free ion energy levels are modified to a great extent. Three theories have been developed to account for these modifications: the crystal field, the ligand field, and the molecular orbital theories. The difference among them arises from assigning to chemical bonding and purely electrostatic effects different relative importance.

In crystal field theory, the paramagnetic ion is considered as being affected only by electrostatic effects. The unpaired electrons

are described by atomic orbitals which are considered not to overlap those of the surrounding ions. The influence of the environment is then reduced to evaluating the form of the electrostatic potential produced by the immediate-neighbour ions treated as point charges. In ligand field theory and molecular orbital theory the bonds between the paramagnetic ion and its nearest-neighbours are assumed to have a partial or total covalent nature respectively. The actual bonds in the crystal we consider are not purely ionic and orbitals do overlap to a certain degree. The crystal field approach will be used, however, because it is simpler and explains the results sufficiently well.

Experimental data reveals that the strength of the crystalline field falls into one of three groups: strong, medium and weak fields. The notations strong, medium, or weak refer to the order of magnitude of the crystalline field relative to the other terms in the Hamiltonian. The relative order of magnitude will decide at what point in the calculations the crystalline field will be used as a perturbation.

The assumptions made in crystal field theory imply that the electrostatic potential  $\beta_c$  at the paramagnetic ion due to its surrounding nearest-neighbours is a solution of Laplace's equation.

$$\nabla^2 \phi_c = 0 \qquad (II.16)$$

The term due to the crystal field term V will be

$$V = \sum_{i} - e \ \beta_{c}(r_{i}, \ \theta_{i}, \ \phi_{i}), \qquad (II.17)$$

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where  $p_c(r_i, \theta_i, \phi_i)$  is the potential at the i<sup>th</sup> electron, and the summation is over all the electrons in the unfilled orbital. The electron orbitals are generally expressed in terms of spherical harmonics, and it becomes especially useful to expand the potential  $p_c$  in a series of them also:

$$\phi_{c}(r, \theta, \phi) = \sum_{n,m} A_{n}^{m} r^{n} Y_{n}^{m}(\theta, \phi)$$
(II.18)

or

$$\phi_{c}(r, \theta, \phi) = \sum_{n,m} U_{n}^{m}$$
(II.19)

in which

$$U_n^{o} = A_n^{c} Y_n^{o}(\theta, \phi) \qquad (II.19a)$$

and

$$U_{n}^{[m]} = [A_{n}^{m} Y_{n}^{m} (\theta, \phi) + A_{n}^{-m} Y_{n}^{-m} (\theta, \phi)] \qquad (II.19b)$$

The normalized harmonics  $Y_n^m(\theta, \phi)$  are defined as

$$Y_{n}^{m}(\theta, \phi) = (-1)^{n} \left[ \frac{1}{4\pi} \frac{(2n+1)(n-|m|)!}{(n+|m|)!} \right]^{1/2} \cdot P_{n}^{m}(\cos \theta) e^{-im\phi}. \quad (II.20)$$

It is not necessary to consider all the terms in the expansion of the  $p_c$ , since symmetry properties of the ion site in the crystal and the configuration of the ion involved reduce the number of terms considerably. The wave functions  $\psi_{p}^{m}$  of the d electrons are expansions in spherical harmonics of order 2. The matrix elements of the potential terms are of the form

$$\int \Psi_{l}^{m*} U_{n}^{m} \Psi_{l}^{m} dt , \qquad (II.21)$$

which integrals vanish for  $n > 2 \$ , where in the case of d electrons  $\ell = 2$ . This occurs because the expansion of  $(\Psi_{\ell}^{m})^{2}$  involves spherical harmonics of order not exceeding  $2\ell$ , and the orthogonality of spherical harmonics then assures zero matrix elements if  $n > 2 \ell$  or n > 4 in the case of d-electrons. All matrix elements of  $U_{n}^{m}$  for which n is odd vanish because the electron wave functions are invariant under an inversion transformation, but the  $U_{n}^{m}$  for odd n change sign. The matrix element for  $U_{0}^{m}$  is just a constant which shifts all levels equally. Further reductions can be obtained if one takes into account the symmetry of the crystalline field. In the particular case of trigonal symmetry studied, the only terms included are m = 0 and  $m = \pm 3$ . Hence the crystal field potential is given by

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where

$$U_n^m = B_n^m V_n^m \qquad (II.22a)$$

The  $V_n^m$  in Cartesian coordinates and the  $B_n^m$  in terms of the  $A_n^m$  are given by Al'tshuler and Kozyrev<sup>11</sup>, and are listed in table II.1 and II.2 respectively.

TABLE II.1

$$V_2^{o} = 3 z^2 - r^2$$
  
 $V_4^{o} = 35 z^4 - 30 r^2 z^2 + 3r^4$   
 $V_4^{3} = (x^2 - 3y^2) x z$ 

TABLE II.2

$$B_{2}^{0} = \frac{1}{4} \sqrt{\frac{5}{\pi}} A_{2}^{0}$$

$$B_{4}^{0} = \frac{3}{16\sqrt{\pi}} A_{4}^{0}$$

$$B_{4}^{3} = \frac{3}{4} \sqrt{\frac{35}{\pi}} |A_{4}^{3}|$$

II.4 The Spin-Hamiltonian

The Hamiltonian, in the general form given in Eq. (II.10)

is exceedingly difficult to work with. Abragam and Pryce<sup>10</sup> arrive at a much simpler expression by applying perturbation theory. First the crystal field potential is expressed in Cartesian coordinates using table II.1. Next we apply the Wigner-Eckart Theorem, which states that if two vector operators transform in the same way under rotations, then the matrix elements are proportional. This allows us to replace the coordinate operators with equivalent angular momentum operators; thus  $x \to L_x$ ,  $y \to L_y$ ,  $z \to L_z$ , etc.; and products such as xy are replaced by  $\frac{1}{2}(L_x L_y + L_y L_x)$ , because of the commutation rules for angular momentum operators. It is only necessary to evaluate the constant of proportionality for one matrix element. The remaining terms in the Hamiltonian (II.10) are transformed into expressions involving the appropriate angular momentum operators  $\underline{L}$ ,  $\underline{S}$  and  $\underline{J}$ .

One is primarily interested only in the lowest level and levels removed from it by no more than a few hundred wave numbers, for higher levels are not occupied at the usual experimental temperatures. This means that one need only consider those levels which arise from the lowest levels of the first two interactions  $V_F + V$ by the remaining perturbations in (II.10). Abragam and Pryce did second order perturbation calculations, working out matrix elements between the ground state and excited states. An expression involving <u>S</u> and <u>I</u> is obtained which is called the 'Spin-Hamiltonian' and takes the form

 $\mathfrak{K}_{s} = \beta \underline{H}_{o} \cdot \underline{g} \cdot \underline{S} + S \cdot \underline{D} \cdot \underline{S} + \underline{S} \cdot \underline{A} \cdot \underline{I} + \text{other nuclear terms and constants}$ (II.23)

 $\underline{\underline{B}}, \underline{\underline{A}}$  and  $\underline{\underline{D}}$  are second-rank symmetric tensors, and  $\underline{\underline{S}}$  is now the 'effective spin operator' whose value is determined by putting the multiplicity of the ground state equal to (2S + 1).

The first term in Eq. (II.23) is the Zeeman term. The g, which now takes the place of the usual spectroscopic splitting factor, is a symmetric tensor whose elements are composed of the free-electron g-value plus an anisotropic correction due to spin-orbit coupling. The second term arises from the zero-field splittings of the ground state in the noncubic crystal field. The splitting is caused in part by the spin-orbit coupling and spin-spin contributions in an unsymmetrical crystal field. This term gives rise to what is generally called the fine structure. The third term gives rise to the hyperfine structure. A difference in the principal values of  $\underline{\underline{A}}$  or  $\underline{\underline{D}}$  indicates an anisotropy of the hyperfine or fine structure respectively. In most cases, the symmetry of  $\underline{g}$  and  $\underline{A}$  is intimately related to the symmetry of the environment. In some cases  $\underline{g}$  and  $\underline{A}$  are diagonal in the same system of co-ordinates, but this may not always be the case. A system of co-ordinates can always be found in which  $\underline{g}$  and  $\underline{\underline{D}}$  are both diagonalized simultaneously.

Usually it is only necessary to take perturbation calculations to second order to find a spin-Hamiltonian which describes the experimental observations. In the case of S-state ions, in which L = 0, second order calculations predict that the crystal field will not split the orbital degeneracy. However, experiments show there is a splitting. It is only by going to high orders in perturbation theory, and considering

spin-orbit interactions simultaneously, that the splitting of the orbital degeneracy in S- state ions can be accounted for. To account for the anomalously high hyperfine splittings found in  $Mn^{2+}$ , it is necessary to consider configuration interactions which admixes to the  $3s^2 3d^5$  some  $3s 3d^5 4s$ .

A spin-Hamiltonian which describes an S- state ion in an electric field of axial symmetry is given by  $Pryce^{12}$ .

$$\mathcal{K}_{s} = \beta \left[ g_{\parallel} + \frac{1}{z} +$$

Here for a trigonal case u, v, w, are mutually perpendicular axes, with respect to which the z-axis is positioned in the [111] direction.

Another suitable spin-Hamiltonian for the system studied is the one used by Vinokurov et al. $^{13}$  in the study of Mn $^{2+}$  in Apatite.

$$\mathfrak{K}_{s} = \beta \left[ g_{\parallel} \right] \left[ \begin{array}{c} H_{z} \left[ S_{z} + g_{\perp} \left( H_{x} \left[ S_{x} + H_{y} \left[ S_{y} \right) \right] \right] \right] \\ + \frac{1}{3} \left[ b_{2} \left[ 0_{2} \right] \left[ + \frac{1}{60} \left[ b_{4} \left[ 0_{4} \right] \left[ 0_{4} \right] \left[ + \frac{1}{60} \left[ b_{4} \right] \left[ 0_{4} \right] \right] \right] \\ + A \left[ S_{z} \left[ I_{z} + B \left( S_{x} \left[ I_{x} + S_{y} \left[ I_{y} \right] \right] \right] \right] \right] \right]$$
(11.25)

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The  $O_n^m$  are functions of the spin operators listed by  $Orbach^{14}$ , and the  $O_n^m$  needed for substitution in Eq. (II.25) are given in table (II.3). The relation between the various parameters in Eqs. (II.25), (II.24) and (II.22a) are given in table (II.4)

#### II.5 Eigenvalues of the Spin-Hamiltonian

The spin-Hamiltonian to which the experimental data has been fitted in this work is Eq. (II.25). To determine the eigenvalues of this Hamiltonian exactly it would be necessary to solve a secular equation of order 36. By applying perturbation theory, however, the problem can be considerably reduced. A transformation is first made to a coordinate system whose Z axis, oriented at ( $\beta$ ,  $\alpha$ ) relative to the crystal field axes, is the quantization axis of the electron spin. The Zeeman term will then be diagonal in this new system, see Vinokurov et al.<sup>13</sup>. The remaining terms in (II.25) are then applied as perturbations. The eigenvalues resulting from second order perturbation calculations are listed by Quick<sup>9</sup>.

## TABLE II.3

$$o_{2}^{o} = 3 s_{z}^{2} - s(s + 1)$$

$$o_{4}^{o} = 35 s_{z}^{4} - [30 s(s + 1) - 25] s_{z}^{2}$$

$$- 6 s(s + 1) + 3 s^{2}(s + 1)^{2}$$

$$o_{4}^{3} = \frac{1}{4} [s_{z}(s_{+}^{3} + s_{-}^{3}) + (s_{+}^{3} + s_{-}^{3}) s_{z}]$$

TABLE II.4

$$b_2^{o} = 3 B_2^{o} = D$$
  
 $b_4^{o} = 60 B_4^{o} = -\frac{a}{3}$   
 $b_4^{3} = 60 B_4^{3} = \frac{20\sqrt{3}}{3}$  a

## CHAPTER III

### PROPERTIES OF CRYSTAL

#### III.1 Introduction

At first attempts were made to grow synthetic  $Mg(OH)_2$  crystals by the slow diffusion method. The apparatus was the same as that described by Quick <sup>9</sup>. The method proved unsuccessful, however, because the high insolubility of  $Mg(OH)_2$  caused it to precipitate instead of crystallize. Dr. F. Holuj kindly supplied some brucite, natural  $Mg(OH)_2$ , which originated in Quebec. A preliminary E.P.R. investigation revealed a characteristic thirty line spectrum of  $Mn^{2+}$  suitable for more detailed studies.

#### III.2 Crystallography

The crystal structure of brucite was first determined by Aminoff<sup>15</sup>, in 1919, to be of the hexagonal  $(CdI_2)$  type, with space group P 3 m 1. The unit cell is trigonal and contains one formula unit. As shown in Fig. III.1, brucite consists of hydroxyls arranged in hexagonal close-packed type of arrangement, with Mg ions occupying slightly distorted octahedral sites only between alternate layers of hydroxyls. It was not until 1956 that the location of the hydrogen ions associated with each oxygen ion was determined by Elleman and Williams<sup>16</sup>.

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Fig. III.1. Structure of brucite showing hexagonal arrangement of ions



Fig. III.2. Structure of brucite projected on (0 0 0 1) plane - - - gives outline of a unit cell

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The distance C between successive Mg planes, which are perpendicular to the c-axis, is  $4.73\text{\AA}$ , as shown in Fig. III.1. The O ions are arranged in hexagonal patterns in planes perpendicular to the C-axis. There are O planes located  $1.04\text{\AA}$  above and below each Mg plane. With each O ion is associated a H ion, lying on a line through the O ion parallel to the c-axis and at a distance of  $0.98\text{\AA}$  removed from it. The adjacent hydroxyl layers are held together by weak Van der Waal's forces.

In a given Mg plane, the six nearest Mg ions surrounding a Mg ion are located at the corners of a regular hexagon, as shown in Fig. III.2. The distance between adjacent Mg ions is 3.12Å. As shown in Fig. III.1, an Mg ion is surrounded by six O ions situated at the corners of a near-perfect octahedron, compressed slightly along [O O O 1]. The Mg-O distance is 2.08Å. The Mn<sup>2+</sup> ions substituted in place of the Mg<sup>2+</sup> ions will have point symmetry D<sub>3d</sub>.

#### III.3 Specimens

Brucite is a relatively soft mineral that cleaves readily to form plates, which, if thin, are colourless. The cleavage plane corresponds to the breaking of the weak Van der Waal's forces between adjacent hydroxyl layers, and thus the c-axis is perpendicular to the plates.

The crystals examined were from the same site in Quebec as those used by Pieczonika et al. $^{17}$  in their earlier study. According to their analysis, the crystal contained 100 parts per million

manganese impurity. All crystals studied exhibited a strong  ${\rm Mn}^{2+}$  spectrum, indicating a high concentration.

#### CHAPTER IV

#### IN STRUMENTATION

The E.P.R. spectrometer was a straight bridge type, using a magic T. A block diagram is shown in Fig. IV.1 The microwave power was supplied by a Varian Model VA 98 M klystron. The static magnetic field was generated with a 12 inch Varian magnet, with 3.5 inch gap, whose power supply was controlled by a Fieldial Model V-FR2503 control unit.

Magnetic field modulation at 100 KHz was generated by an oscillator built into the Princeton Applied Research (P.A.R.) Model JB-5 Lock-in Amplifier. This signal was amplified externally and applied to two coils connected in series and mounted external to the cooling cryostat. The magnetic resonant absorption signal from the cavity was detected by the crystal detector. The resonant signal was pre-amplified and then fed into the P.A.R. Lock-in Amplifier, which compares the phase and frequency of the resonant signal with the original 100 KHz modulation signal. The result is a derivative signal proportional to the resonant signal, which can be displayed on the oscilloscope or chart recorder as a function of magnetic field. To allow display on the oscilloscope the magnetic field is modulated at 60 Hz, in addition to 100 KHz.

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The klystron frequency was stabilized to the cavity resonant frequency using a Teltronic Model KSLP Klystron Stabilizer. The stabilizer works on the principle of automatic-frequency control (A.F.C.). A sine wave modulation of approximately 70 KHz was impressed on the reflector voltage, thus causing a small amount of frequency modulation. If the klystron frequency is tuned at or near the cavity resonant frequency, the output detected by the A.F.C. detector will contain a 70 KHz component. The A.F.C. signal is amplified and then applied to the phase-sensitive detector (P.S.D.), built into the stabilizer, which compares the signal with the original modulation signal. The result is a D.C. error voltage with a polarity and magnitude proportional to the difference between the klystron oscillator frequency and the resonant frequency of the cavity. The error voltage is applied to the reflector of the klystron in such a manner that the klystron frequency is pulled back to the frequency of the cavity.

The cavity, which operated in the TEOll mode , had been used successfully in this laboratory before, and is illustrated in Fig. IV.2. It was constructed out of pyrex glass. The glass was first coated with a baked-on layer of silver oxide, and then a thin layer of gold was sputtered on. An outer cup of plastic, sealed with glycerine, was used to exclude the cooling liquid nitrogen from the cavity. Heat was applied to the cavity by a coil of chromel heating wire at the base of the cavity, inside the outer cup. An Electro Model B Filtered D.C. Power Supply was used to energize the heater

coils. The crystal was glued by epoxy on a quartz glass pin, which in turn was glued to the crystal rotation device at the side of the cavity. A copper-constantan thermocouple ran up from the base of the cavity and was glued to the bottom of the crystal. The temperature was monitored with a Leeds and Northrup. 8686 Millivolt Potentiometer.

# CHAPTER V

### EXPERIMENTAL PROCEDURE

### V.1 Orientation of the Crystal

A major problem which had to be overcome, before the study of the temperature variation of the spectrum could begin, was orientation of the crystal on the quartz pin. It was desirable to take precise measurements of the resonant, fields along the magnetic z-axis, perpendicular to the z-axis and at an intermediate orientation in a symmetric magnetic plane. The three symmetric magnetic planes in the crystal are planes through the z-axis, which are related by rotations of only  $60^{\circ}$  (rather than  $120^{\circ}$ ) about the z-axis for magnetic fields at an arbitrary angle with the z-axis. To permit the precise measurements to be made, it was necessary to orient the crystal on the pin in such a manner that the three desired orientations could be reached by a rotation of the magnet and, at most, a very small orientation of the crystal inside the cavity. This was found to be necessary because, once the thermocouple was glued onto the crystal, use of the crystal rotation device was limited to approximately 15° to 20°. If rotations greater than this were attempted, the 'Q' of the cavity was reduced and klystron frequency stabilization became impossible, or the quartz pin fractured due to stresses applied to it by the thermocouple. It was possible by visual

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observation to estimate the c-axis of the crystal, which was perpendicular to the cleavage plane. However, there were no other distinguishable surfaces to aid orientations.

From the earlier work of Pieczonka et al. , it had been determined that the magnetic z-axis corresponded to the crystallographic c-axis. The crystal was glued temporarily with the  $\hat{z}$ -axis perpendicular to the pin, alignment being done visually. An angular variation study was carried out to locate exactly the z-axis, which corresponded to the direction in the crystal along which the applied magnetic field causes maximum spread of the observed spectrum. Using a stereographic plot to determine magnet and crystal rotations, an angular variation was carried out in which the applied magnetic field formed a cone.  $45^{\circ}$  relative to the z-axis. This study allowed a determination of the magnetic symmetric planes. Once these had been determined relative to the temporary alignment, the crystal was permanently glued with a new alignment such that the three desired orientations could be reached with a minimum of crystal rotation. The new alignment was verified to be satisfactory by a new angular variation study and then the thermocouple was glued to the crystal.

# V.2 Temperature Variation

Precise measurements of specific lines at all three orientations were taken at approximately 20  $K^{\circ}$  intervals from liquid nitrogen to room temperature. The current through the heater wire was adjusted to an arbitrary value and the apparatus allowed to come

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to equilibrium for about an hour to hour and one half. Once equilibrium was reached, it was found that as long as the current was maintained constant the thermocouple readings indicated a temperature fluctuation of no greater than  $\pm 1 \text{ K}^{\circ}$ . The current was monitored closely throughout a set of readings and adjusted if necessary. No attempt was made to accurately calibrate the thermocouples and an estimated error due to the thermocouples is  $\pm 1 \text{ K}^{\circ}$ . The reference temperature used was liquid nitrogen.

### V.3 Measurement of Magnetic Field

As in most E.P.R. studies the frequency of the incident microwave radiation was held constant and the applied magnetic field H was swept slowly through the resonance absorption spectrum. To calculate the spin-Hamiltonian parameters, it is necessary to know accurately the frequency of the microwave radiation and the strength of the applied magnetic field at which an absorption takes place.

The value of the magnetic field was measured using a proton resonant probe, commonly called an N.M.R. probe, attached to one poleface of the magnet. The outputs of the N.M.R. probe and the P.A.R. Lock-in Amplifier were fed through an electronic switch and superimposed on an oscilloscope screen. When the two signals were properly aligned on the screen, the frequency of the N.M.R. probe could be read off the frequency counter Due to the inhomogeneity of the magnetic field between the poleface and the location of the specimen at the center of the gap, a correction

must be made to obtain the frequency the N.M.R. probe would read if placed at the specimen location. The corrected frequency is obtained by taking away from the frequency at the poleface a correction, given in Fig. V.1. The condition of resonance for the protons in the N.M.R. probe is

$$h v_{\rm p} = \gamma \beta_{\rm N} H \tag{V.1}$$

where  $v_{p}$  is the proton resonant frequency,  $\gamma$  is the gyromagnetic ratio of the proton and  $\beta_N$  is the nuclear magneton. Rearranging Eq. (V.1) and making numerical substitutions for the constants, the magnetic field at the specimen is given by

$$H(K - gauss) = \frac{1}{4.25759} v (mc/sec) (V.2)$$

where v is the corrected frequency. An estimate of the error due to inhomogeneity of the magnetic field is approximately  $\pm$  0.2 gauss.

# V.4 Use of Magnetic Field Marker

The frequency of the microwave radiation supplied by the K-band ( $\sim 23.4 \text{ CH}_2$ ) klystron determines the magnetic field at which the resonant signal of the diphenyl picryl hydrazyl (DPPH) free radical occurs. DPPH was used as a magnetic field marker because its g-factor, 2.0036, is independent of temperature and direction of the applied magnetic field.





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#### CHAPTER VI

#### CALCULATIONS AND RESULTS

VI.1 Calculations of Magnetic Fields at which Resonance Occurs

The equations for the energy levels, as explained in Sec. II.5, are given by  $Quick^9$ . For resonance to occur the equation

 $\Delta E = E(M, m) - E(M - 1, m) = h_{\Psi}$  (VI.1)

must be satisfied. Here M, the spin quantum number, and m, the nuclear quantum number, have the values - 5/2, - 3/2, - 1/2, 1/2, 3/2, 5/2. Only allowed electronic transitions were considered, for which  $\Delta m = 0$ ,  $\Delta M = \pm 1$ . For a given transition  $\Delta E$  takes the form

 $\triangle E = E(M, m) - E(M - 1, m) = g \beta H(M, m \rightarrow M - 1, m) + C(in ergs)$ (VI.2)

Here C is an expression in units of ergs, which involves the spin-Hamiltonian parameters, the transition energy, and depends on the direction but not the magnitude of the applied magnetic field. The resonant condition Eq. (VI.2) has been given in units of energy (ergs) and our measurements were taken in terms of the magnetic field positions (gauss) of the absorption signals. Combining the resonant condition for DPPH and Eqs. (VI.1) and (VI.2) we obtain

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$$g_d \beta H_d = \Delta E = g \beta H(M, m \rightarrow M - 1, m) + C (ergs)$$
 (VI.3)

where  $g_{\rm d}$  is the g-factor of DPPH. Dividing both sides of Eq. (VI.3) by  $g\beta$  and rearranging we obtain

$$H(M, m \rightarrow M - 1, m)(gauss) = \frac{g_d H_d}{g} - \frac{C(ergs)}{g\beta} = \frac{g_o}{g} \left[\frac{g_d H_d}{g} - \frac{C(ergs)}{g_o\beta}\right] \quad (VI.4)$$

where  $g_0$  is the g of the free electron. The division of C(ergs) by  $g_0\beta$  just converts this expression to one in units of gauss. The term  $\frac{g_d^H d}{g_0}$  is denoted by H<sub>0</sub>, the magnetic field at which the absorption for the free electron occurs. Therefore Eq. (VI.4) becomes

$$H(M, m \to M - 1, m) = \frac{g_0}{g} [H_0 - C(gauss)]$$
 (VI.5)

The equations for the magnetic fields at which the various resonances occur are given in Table VI.1a. The constants  $a_n^{m+}$  have been listed by Vinokurov et al.<sup>13</sup>, however, errors appear in the publication. Corrected  $a_n^{m+}$  appear in Table VI.1b. These formulas were used in a computer program, given in Appendix B, to generate the resonant fields.

# VI.2 Fitting the Spin-Hamiltonian Parameters

It was hoped in the experiment to fit the seven spin-Hamiltonian parameters  $g_{||}$ ,  $g_{\perp}$ , A, B,  $b_2^{\circ}$ ,  $b_4^{\circ}$ ,  $b_4^{3}$ . To accomplish

this, a least squares process, as outlined by Malchikov et al.<sup>18</sup>, was used.

The principle involved was to minimize the expression

$$\sum_{j=1}^{NHX} [HX(j) - HC(j)]^2 = \sum_{j=1}^{NHX} W_j^2$$
(VI.6)

where NHX was the number of experimental lines fitted, HX(j) was the experimental field measured, and HC(j) was the field calculated using a set of trial parameters P(i), i = 1, 7. If  $\sum_{j=1}^{NHX} W_j^2$  was to be a minimum, then the partial derivative of Eq. (VI.6) with respect to each of the parameters must equal zero. If we expand HC in a Taylor's series in terms of the P(i)'s before we differentiate, the result is a set of NHX linear equations with respect to seven unknowns. The seven unknowns are the corrections, COR(j), to be made to the seven trial parameters to reduce  $\sum_{j=1}^{NHX} W_j^2$  to a minimum. The coefficients of the corrections involved partial derivations, D1(j, i), of the HC(j) with respect to each of the parameters. In operator notation, the equations take the form

$$W = D \mathbf{1} \cdot C O R \tag{VI.7}$$

Since Eq. (VI.7) is not a set of exact equations, the 'best' solution involved a least squares problem. This necessitated minimizing the Euclidean norm of

Values of magnetic field at which resonance occurs for constant frequency

$$\begin{split} \mathrm{H}(\pm \frac{5}{2}, \ \mathrm{m} \leftrightarrow \pm \frac{3}{2}, \ \mathrm{m}) &= \frac{g_{0}}{\mathrm{g}} \left[\mathrm{H}_{0} \mp 4a_{2}^{0} \mp 4a_{4}^{0}\right] \\ &- \frac{1}{\mathrm{H}_{0}} \left\{ \begin{array}{l} \frac{8}{9} \left|a_{2}^{1}\right|^{2} - \frac{4}{9} \left|a_{2}^{2}\right|^{2} - \frac{1}{40} \left|a_{4}^{1}\right|^{2} + \frac{1}{20}\right| \left|a_{4}^{2}\right|^{2} \right] \\ &+ \frac{1}{120} \left|a_{4}^{3}\right|^{2} + \frac{1}{2} \left|a_{2}^{1}\right| \left(a_{4}^{1-} + a_{4}^{1+}\right) \right] \\ &+ \frac{1}{2} \left[a_{2}^{2}\left(a_{4}^{2-} + a_{4}^{2+}\right) \pm \left[2a_{2}^{1} + \left(a_{4}^{1-} + a_{4}^{1+}\right)\right] \left(a_{2}^{\frac{B^{2}-A^{2}}{2K}}\right) \sin 2\beta \\ &+ \frac{1}{4}\left(\frac{35}{4} - \mathrm{m}^{2}\right)\left(\frac{A^{2}\mathrm{B}^{2}}{\mathrm{K}^{2}} + \mathrm{B}^{2}\right) + \frac{1}{2} \mathrm{m}^{2}\left(\frac{B^{2}-A^{2}}{2\mathrm{K}}\right)^{2} \sin^{2} 2\beta \\ &\pm 2\mathrm{m} \left[\frac{\mathrm{AB}^{2}}{\mathrm{K}}\right] - \mathrm{m} \mathrm{K} \right] \\ \mathrm{H}(\pm \frac{3}{2}, \ \mathrm{m} \leftrightarrow \pm \frac{1}{2}, \ \mathrm{m}) &= \frac{g_{0}}{\mathrm{g}} \left[\mathrm{H}_{0} \mp 2a_{2}^{0} \pm 5a_{4}^{0} \\ &- \frac{1}{\mathrm{H}_{0}} \left\{-\frac{1}{9} \left|a_{2}^{1}\right|^{2} + \frac{5}{9}\left|a_{2}^{2}\right|^{2} + \frac{1}{5}\left|a_{4}^{1}\right|^{2} + \frac{9}{80}\left|a_{4}^{2}\right|^{2} - \frac{1}{120}\left|a_{4}^{3}\right|^{2} \\ &+ \frac{1}{20}\left|a_{4}^{4}\right|^{2} - \frac{1}{2} \left[a_{2}^{1}\left(a_{4}^{1+} + a_{4}^{1-}\right) + \frac{1}{4} \left[a_{2}^{2}\left(a_{4}^{2+} + a_{4}^{2-}\right)\right] \\ &\pm \left[a_{2}^{1} - \frac{5}{4}\left(a_{4}^{1-} + a_{4}^{1+}\right) \mathrm{m}\left(\frac{B^{2}-A^{2}}{2\mathrm{K}}\right) \sin 2\beta + \frac{1}{4} \left(\frac{35}{4} - \mathrm{m}^{2}\right) \\ &\times \left(\frac{A^{2}\mathrm{B}^{2}}{\mathrm{K}^{2}} + \mathrm{B}^{2}\right) + \frac{1}{2} \mathrm{m}^{2}\left(\frac{B^{2}-A^{2}}{2\mathrm{K}}\right)^{2} \sin^{2} 2\beta \pm \mathrm{m} \frac{\mathrm{AB}^{2}}{\mathrm{K}}^{2} - \mathrm{m} \mathrm{K}^{2} \right] \end{split}$$

$$\begin{aligned} H(\frac{1}{2}, \ m \rightarrow -\frac{1}{2}, \ m) &= \frac{g_{o}}{g} \left[ H_{o} - \frac{1}{H_{o}} \left\{ -\frac{4}{9} \left| a_{2}^{1} \right|^{2} + \frac{8}{9} \left| a_{2}^{2} \right|^{2} \right. \right. \\ &\left. - \frac{1}{4} \left| a_{4}^{1} \right|^{2} - \frac{1}{10} \left| a_{4}^{2} \right|^{2} + \frac{1}{60} \left| a_{4}^{3} \right|^{2} + \frac{1}{3} \left| a_{2}^{1} \left( a_{4}^{1+} + a_{4}^{1-} \right) \right. \right. \\ &\left. - \left| a_{2}^{2} \left( a_{4}^{2+} + a_{4}^{2-} \right) + \frac{1}{4} \left( \frac{35}{4} - m^{2} \right) \left( \frac{A^{2}B^{2}}{K^{2}} + B^{2} \right) \right. \\ &\left. + \left. \frac{1}{2} \left. m^{2} \left( \frac{B^{2}-A^{2}}{2K} \right)^{2} \left. \sin^{2} \left. 2\beta \right. \right\} - m K \right] \end{aligned}$$

Here

$$g^{2} = g_{\parallel}^{2} \cos^{2} \theta + g_{\perp}^{2} \sin^{2} \theta$$
$$K^{2} g^{2} = A^{2}g_{\parallel}^{2} \cos^{2} \theta + B^{2}g_{\perp}^{2} \sin^{2} \theta$$

$$\tan \beta = \frac{g_{\perp}}{g_{\parallel}} \qquad \tan \theta$$

 $\alpha = \emptyset$ 

where  $\theta$  and  $\beta$  are the spherical coordinates describing the direction of the magnetic field with respect to the crystal axes.

# TABLE VI.1b

Corrected  $a_n^{m \pm}$ , used to calculate resonant fields.  $a_4^{1 \pm} = \frac{1}{4} [20 b_4^0 \sin \beta \cos \beta(3 - 7 \cos^2 \beta)$   $+ b_4^3 \{\sin^2 \beta(4 \cos^2 \beta - 1) \cos 3 \alpha$   $\mp i 3 \sin^2 \beta \cos \beta \sin 3 \alpha \} ]$   $a_4^{3 \pm} = \frac{1}{4} [-140 b_4^0 \sin^3 \beta \cos \beta + b_4^3 \{\cos 3 \alpha (4 \cos^4 \beta)$   $+ 3 \cos^2 \beta - 3)$   $\pm i \cos \beta(5 - 9 \cos^2 \beta) \sin 3 \alpha \} ]$  $a_4^{4 \pm} = \frac{1}{8} [35 b_4^0 \sin^4 \beta + b_4^3 \{-\sin \beta \cos \beta(3 + \cos^2 \beta) \cos 3 \alpha)]$ 

 $\pm$  i sin  $\beta(\cos^2 \beta + 1) \sin 3 \propto \}]$ 

$$W - D \mathbf{1} \cdot C O R \qquad (VI.8)$$

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The program used to accomplish this was 'Subroutine LLSQ', from the Scientific Subroutine Package of the I.B.M. 360 computer. A printout of the program is given in Appendix C.

In practice, it was found necessary to repeat this procedure several times. After each iteration, the fit improved and the corrections to the parameters became smaller. In most cases, no further improvement was obtained after four iterations. The program which accomplishes the iterations is given in Appendix A.

# VI.3 Results At X-Band

A qualitative room temperature angular variation study performed at X-band confirmed the results published previously by Pieczonka et al.<sup>17</sup>. An investigation at liquid nitrogen temperature revealed that the spectrum was significantly different than that at room temperature. A typical recording for H parallel to the crystallographic c-axis,  $[0 \ 0 \ 0 \ 1]$ , at liquid nitrogen temperature is shown in Fig. VI.1a. A reduction of the temperature to that of liquid helium failed to alter the spectrum appreciably from that of liquid nitrogen temperature, as revealed by comparing Fig. VI.1a and Fig. VI.1b. The slight variation in the observed spectrum indicates that the spin-Hamiltonian parameters change little below liquid nitrogen temperature.



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# VI.4 Results at K-Band

In the K-band study precise measurement of resonant fields were made at three orientations in the temperature range from liquid nitrogen to room temperature. Typical recordings of the spectrum for H parallel and perpendicular to the crystallographic c-axis are shown in Fig. VI.2 and Fig. VI.3, for room and liquid nitrogen temperatures respectively. A typical spectrum for brucite can be thought of as consisting of 6 groups of 5 lines, one group corresponding to each of the nuclear spin states. The five lines correspond to the 5 possible electron spin transitions with  $\triangle M = \pm 1$ . The variation of the spectrum with temperature is primarily due to the change of the spacing of the 5 lines in each group. Angular variations of the spectrum are given in Fig. VI.4. The spectrum was isotropic for rotations of H in the  $(0 \ 0 \ 0 \ 1)$  plane, and was symmetrical about the  $[0 \ 0 \ 0 \ 1]$  axis for rotations of H in the  $(1 \ 0 \ \overline{1} \ 0)$  plane. The angular variation taken in a cone about the c-axis, as given in Fig. VI.4c, illustrates the 60° separation of the symmetric magnetic planes. Fig. VI.5 shows the relationship between the symmetric magnetic planes and the actual ion site. No other arbitrary planes through the c-axis exhibit symmetry for rotations of H in the plane.

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The resonant fields for a set of measurements taken at room temperature are given in Table VI.2. An estimated error in the measured resonant fields is  $\pm$  2.0 G due to poor resolution of the spectrum. The calculated values in Table VI.2 are generated by the parameters that have been fitted, as described in Sec. VI.2.











Fig. VI.4a. Angular variation of spectrum for rotation of H in (10TO) plane T = 295°K. The crosses are experimental measurements which were obtained for microwave frequency 23.4 GHz. The data is listed in Table VI.1. The solid resonant field calculated using the values of the parameters given in Table VI.1.







Fig. VI.4c. Angular variation of spectrum for rotation of H in a cone at 45° to c-axis, obtained using parameter given in Table VI.1. Note that at 30°, 60°, 150°, and 210° the spectrum repeats itself. These correspond to the symmetric planes 'S' given in Fig. VI.5. All other planes are asymmetric and repeat themselves every 120°.



Fig. VI.5. Ion site projected on (0 0 0 1) plane. S relates to symmetric planes given in Fig. VI.4c.

## TABLE VI.2

Position of Resonant Fields at Room Temperature  $(295^{\circ}K)$  and for Microwave Frequency 23.4 GHz. 'Calculated' fields were computed for the Spin-Hamiltonian parameters  $g_{\parallel} = 2.0011 \pm 0.0005$ ,  $g_{\perp} = 2.0010 \pm 0.0005$ ,  $A = -90.74 \pm 0.25G$ ,  $B^{\parallel} = -89.69 \pm 0.25G$ ,  $b_2^{\circ} = -5.85 \pm 0.50G$ ,  $b_4^{\circ} = -4.31 \pm 0.50G$ ,  $b_4^{\circ} = 0 \pm 150G$ .

Direc-	TRANSITION			MAGNETIC FIELDS IN GAUSS		
tion of <u>H</u>	m	M	M <b>-</b> 1	ME AS URE D	CALCULATE D	ERROR
[0001]	-5/2	-3/2	-5/2	8087.7	8089.3	-1.62
	572	1/2	-1/2	8133.7	8134.8	-1.1
	-3/2	1/2	-1/2	8223.2	8223.6	-0.4
	-1/2	1/2	-1/2	8313.7	8313.5	0.2
	1/2	1/2	-1/2	8404.9	8404.2	0.6
	~ / 0	1/2	-1/2	8497.3	8496.0	1.3
	372	5/2	3/2	8534•2	8533.8	0.4
	5/2	-3/2 3/2 1/2	-5/2 1/2 -1/2	8554.3 8576.5 8588.3	8552.9 8576.5 8588.7	1.4 0.0 -0.4
		-3/2 5/2	-1/2 3/2	8598.8 8622.1	8601.0 8624.6	-2.3 -2.5
[1010]	-5/2	3/2 1/2 -1/2	1/2 -1/2 -3/2	8126.1 8137.4 8149.3	8127.3 8137.8 8150.3	-1.2 -0.4 -1.0
	5/2	3/2 1/2 -1/2	1/2 -1/2 -3/2	8574.6 8586.4 8601.5	8571.2 8586.6 8604.0	0.4 -0.2 -2.5
O-45° in		-1/2	-3/2	8121.4	8120.8	0.6
(10TO) plane	-5/2	1/2 3/2	-1/2 1/2	8135.9 8151.9	8134.7 8149.1	1.2 2.8
	5/2	-1/2 1/2 3/2	-3/2 -1/2 1/2	8573.7 8587.3 8602.0	8577.1 8586.2 8595.6	-3.4 1.1 6.3

Graphical presentation of the variation with temperature of the parameters A, B,  $b_2^{0}$  and  $b_4^{0}$  appears in Fig. VI.6. The data from which these graphs were plotted appears in Table VI.3. It was found that the g values remained constant, at  $g_{\parallel} = 2.0011 \pm 0.0005$  and  $g_{\perp} = 2.0010 \pm 0.0005$ , over the temperature range studied. As shown in Fig. VI.6c the results obtained for  $b_4^{0}$  do not appear to follow a consistent trend of increasing or decreasing with temperature. Variations in  $b_4^{3}$  of as much as  $\pm 150$  G had no significant effect on the root mean square (RMS) error of fit.



Fig. VI.6a. A and B vs. temperature





Fig. VI.6c.  $b_4^{o}$  vs. temperature

# TABLE VI.3

Best fit data of spin-Hamiltonian parameters A, B,

 $b_2^{o}$  and  $b_4^{o}$ 

T( <sup>°</sup> k)	A	В	b2°	b <sub>4</sub> °
77	-92.22	-90.18	-13.39	-3.74
92	<b>-</b> 92.24	-90.16	-13.01	-3.33
120	-92.21	-90.19	-12.49	-3.12
144	-92.05	-90.22	-12.90	<b>-</b> 2.64
162	-92.06	-90.13	<b>-12.</b> 52	-2.50
176	-91.96	-90.22	-11.81	-2.74
204	-91.83	-90.09	-12.07	-2.22
218	-91.65	-90.05	-10.98	-1.97
249	-91.51	-89.84	<b>-1</b> 0.04	-2.30
273	-91.75	-89.93	- 8.17	<b>-</b> 3.03
295	-90.74	-89.69	- 5.85	-4.31

### CHAPTER VII

## DISCUSSIONS AND CONCLUSIONS

A significant difference between the parameters found by Pieczonka et al.<sup>17</sup> at X-band appeared as shown in Appendix D. To verify that the discrepancies were not due to the different formulation of the spin-Hamiltonians or method of calculation, Pieczonka's resonant fields were fitted using our routine. Within experimental error the values of the parameters calculated at X-band were the same by both methods. Although the validity of the perturbation theory should be better for the K-band results, it seems unlikely that inclusion of higher order terms for the X-band calculations would significantly reduce the discrepancy. It is possible that the spin-Hamiltonian used was inadequate. It may be necessary to use a generalization of the spin-Hamiltonian method, as given for example by Grant and Strandberg<sup>19</sup>, which includes nonlinear terms in N. It would be of interest to investigate the  $Mn^{2+}$  in Ca(OH)<sub>2</sub> at K-band to see if similar discrepancies appear between the K and X-band results for the isomorphic crystal.

The temperature variation in the parameters found for  $Mn^{2+}$ in brucite exhibits the same trends as observed by Quick<sup>9</sup> for the same ion in the isomorphic crystal Ca(OH)<sub>2</sub>. It was found that the spin of  $b_2^{0}$  changed above approximately 450°K for Ca(OH)<sub>2</sub>. From Fig. VI.6b it appears that a similar sign change might occur in brucite; a further

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study of the spectrum above room temperature is required to verify the sign change and to provide a more complete set of experimental data to compare with theoretical curves.  $b_2^{0}$  is a measure of the axial component of the crystal field. It would be of interest to study the dependence of  $b_2^{0}$  on mechanical stress in samples of brucite subjected to pressure along the C-axis.

An examination of deuterated samples of  $Ca(OH)_2$  would supply additional data for comparison with the isomorphic  $Ca(OH)_2$  and  $Mg(OH)_2$ .

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PURPOSE

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TO CARRY OUT ITERATIONS IN ORDER TO FIT SPIN-HAMIL-TONIAN PARAMETERS, P(I), TO A SET OF EXPERIMENTAL RESONANT FIELDS, HX.

DESCRIPTION OF PARAMETERS DELTA(I)-INCREMENT OF P(I) TO CALCULATE THE PARTIAL DERIVATIVES NEEDED IN SUBROUTINE LLSQ(GAUSS) P(1) -G PARALLEL P(2)-G PERPENDICULAR  $P(\tilde{3})$ -A P(4) -B -b8 P(5)P(6)-b4 P(7) -b NTEMP -NUMBER OF TEMPERATURES AT WHICH READINGS WERE TAKEN NANGLE -NUMBER OF ORIENTATIONS AT A GIVEN TEMPER-ATURE AT WHICH MEASUREMENTS WERE MADE NHX -NUMBER OF RESONANT FIELDS MEASURED AT A GIVEN TEMPERATURE P1(I)'S -TRIAL PARAMETERS(GAUSS) -CALCULATED RESONANT FIELDS HC -EXPERIMENTAL RESONANT FIELDS ΗX D(I,J)-PARTIAL DERIVATIVES W(J)-DIFFERENE BETWEEN HX'S AND HC'S THETAD -ANGLE(DEGREES) DESCRIBING ORIENTATION OF THE MAGNETIC FIELD RELATIVE TO Z-AXIS -ANGLE(DEGREES) DESCRIBING ORIENTATION OF PHI THE MAGNETIC FIELD RELATIVE TO X-AXIS -PROTON RESONANCE FREQUENCY AT WHICH DPPH DPPHF ABSORPTION OCCURS SUBROUTINES REQUIRED (1) SUBROUTINE HNTRIG (2) SUBROUTINE ARRAY (3) SUBROUTINE LLSQ

METHOD

THE TRIAL PARAMETERS ARE USED IN SUBROUTINE HNTRIG TO CALCULATE A SET OF CALCULATED RESONANT FIELDS. THE TRIAL PARAMETERS AND AN INCREMENT ARE USED TO FIND A SET OF PARTIAL DERIVATIVES NEEDED IN SUBROUT-INE LLSQ. LLSQ IS USED TO FIND THE CORRECTIONS, COR(1), TO THE TRIAL PARAMETERS IN ORDER TO MINIM-IZE THE EUCLIDEAN NORM FETTEEN THE CALCULATED FIELDS AND THE EXPERIMENTAL RESONANT FIELDS.

#### С PROGRAM FIT С С DIMENSION THETAD(5), PHID(5), THETA(5), PHI(5), BETA(5), ALPHA(5), DPPHE 1(5), DPPH(5), G(5), GX(5), P(7), P1(7), HXF(5, 5, 6), HX(5, 5, 6), HC(5, 5, 6), H 2D(5,5,6),COR(7),W(30),D(30,7),D1(210),IPIV(7),AUX(14),P2(7),DELTA( (37), SUM1(7), STD(7) С С READ IN PARAMETERS TEMPERATURE, ETC. С READ (5,1) (DELTA(I), I=1,7) READ (5,3) (P1(I), I=1,7) READ(5,72) NTEMP KN=073 READ(5,2) NANGLE,NHX P1(7) = 10.0DO 60 NA=1, NANGLE DO 60 I=1.5DO 60 K=1,660 HXF(NA, I, K) = 0.00DO 4 J=1, NANGLE READ(5,5) THETAD(J), PHID(J), OPPHF(J) THETA(J)=THETAD(J)\*3.141593/180. PHI(J)=PHID(J)\*3.141593/180. DPPH(J)=DPPHF(J)/4.2577 С READ IN THE MEASURED FIELDS GIVEN IN TERMS OF THE PROTON С RESONANT FREQUENCY. С INDEX J IDENTIFIES THE ORIENTATION С INDEX K1 IDENTIFIES THE ELECTRON SPIN TRANSITION С Kl=1, 5/2 to 3/2Kl=2, 3/2 to 1/2С K1=3, 1/2 to -1/2С С Kl=4, -1/2 to -3/2С Kl=5, -3/2 to -5/2INDEX NI IDENTIFIES THE NUCLEAR SPIN С N1=1, 5/2С С N1=2, 3/2С N1=3, 1/2N1=4, -1/2С N1=5, -3/2С С N1=6, -5/2С 7 PEAD(5,6)K1,N1,HXF(J,K1,N1),K2,N2,HXF(J,K2,N2),K3,N3,HXF(J,K3,N3), 1K4,N4,HXF(J,K4,N4),K5,N5,HXF(J,K5,N5),K6,N6,HXF(J,K6,N6),K7,N7,HXF 2(J.K7,N7),N IF(N.EQ.O) GU TU 7 $D0 \ 4 \ 1=1,5$ DO 4 K=1,6 4 HX(J,1,K)=HXF(J,I,K)/4.2577 N=0DO 50 1=1,750 COR(I) = 0.00

8 DO 9 I=1,7 P(I)=P1(I)

9 P1(I)=P(I)+COR(I)

	WRITE (6,10)
	WRITE (6,11)
en en en de la companya de	WRITE $(6, 12)$ (P1(I), I=1,7)
	CALL HNTRIG(P1, NANGLE, THETA, PHI, DPPH, HC)
	WRITE (6,13)
ann ngo a naan naadaan in	<b>J=</b> 0
	DO 14 NA=1, NANGLE
	DO 14 MN=1,6
and an and we do not see the second	DO 14 MS=1,5
	IF(HX(NA,MS,MN)-0.2) 14,15,15
15	J=J+1
	W(J) = HX(NA, MS, MN) - HC(NA, MS, MN)
	WRITE (6,16) NA,MN,MS,HX(NA,MS,MN),HC(NA,MS,MN),W(J)
14	CONTINUE
	SUM=0.0
	DO 17 K=1,NHX
17	SUM=SUM+W(K)**2
	WRITE (6,18) SUM
	IF (SUM-25.0) 19,20,20
<u> </u>	WRITE (6,21)
	N=10
	GO TO 33 ·
20	DO 22 I=1, 7
	$\mathbf{J} = 0$
	DO 51 $K=1,7$
	P2(K)=P1(K)
	P2(1)=P1(1)+DEL1A(1)
	CALL HNIRIG(P2, NANGLE, THETA, PHI, DPPH, HD)
	SUM1(1)=0.0
arastronomia sy control y bits communi (2012). So y	DU 22 NA=I, NANGLE
•	UU 22 MN=1,6
	UU 22 MST1+9 TE ANMANA NE MAN D 20 22 22
	17 (11X(10A,105,100)-0.2) (22,23,23)
2.5	
•	D(J+1) = HU(NA+MS+MN)/DETTA(T) = HU(NA+MS+MN)/DETTA(T)
د. در زر	SUM(1) = SUM(1) + U(J(1) + U(J(1)))
£. Z	
75	CONTINUE CONTINUE
()	
(	C ARRANGES PARTIAL DERIVATIVES IN LINEAR FORM IN ORDER THAT
, (	THE SCIENTIFIC SUBROUTINE LLSQ MAY BE ENTERED
Č	
· · · · · · · · · · · · · · · · · · ·	CALL ARRAY(2, NHX, 7, 30, 7, D1, D)
	CALL LLSO(D1,W,NHX,7,1,COR,IPIV,0.0000C2,IERF,AUX)
· · · · · · · · · · · · · · · · · · ·	IF (IERR) 24,25,26
24	WRITE (6,27)
· · · · · · · · · · · · · · · · · · ·	N = 1.0
	GO TO 33
- 26	WRITE (6,22) IERR
25	WRITE (6,29)
	WRITE $(6, 41)$ (AUX(J), J=1, 14)
	WR1TE(6,40)
· * -: -:	WRITE(6,11)

,
· · · · ·	WRITE(6,41) (SUM1(1),I=1,7)			
	WRITE(6,71)			
	WRITE(6,11)			
	WRITE(6,41) (STD(I), I=1,7)			
	WRITE (6.31)			
	WRITE (6,11)			
n na an	WRITE $(6,3)$ (COR(I), I=1,7)	n an	na se an	an a
33	N=N+1			
	IF (N.LT.4) GO TO 8			
	KN=KN+1			
	IF (KN.LT.NTEMP) GO TO 73			
1	FORMAT (7F8.4)			
2	FORMAT (213)	an a	a second and a second and a second as a	n in the second s
3	FORMAT (1H0,7F10.5)			
5	FORMAT (2F5.1, F8.2)			
6	FORMAT (7(212, F7.1), 12)			•
10	FORMAT (45H1		PARAMETI	ERS)
. 11	FORMAT (67HO GPAR GPE	Α	8	820 B
1999 - 1999 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -	140 B43)	n en an an en	and the state of the states	
12	FORMAT (1H0,7F10.5)			
13	FORMAT (60HO NA MN )	4S HX	•	HC
	1 W)			
16	EORMAT (1H0,316,3F15.2)			
18	FORMAT (5HOSUM=,F10.4)			
21	FORMAT (34HO	FIT COMPL	ETE)	
27	FORMAT (42HO IERR NEGATI	IVE PROGRAM	1 TERMINATED	)
28	FORMAT (36HO		RANK = 121	į
29	FORMAT (36HO	AUX M	ATRIX)	
40	FORMAT (60H0	SUM OF SC	UARES OF PAR	RTIAL DERIVAT
	1 IVES)			
41	FORMAT(1H0,1P7E10.3)			
31	FORMAT (53HO	· C C	RRECTION TO	PARAMETERS)
7.1	FORMAT(57HO	STANDAR	O DEVIATION	OF PARAMETER
	15)			
72	FORMAT (13)			
	CALL EXIT			
	END			a san a sa anna a na a

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C SUBROUTINE HNTRIG	
C PURPOSE C TO GENERATE A SET OF RESONANT FIELDS, H(I,J,K), C USING A SET OF TRIAL PARAMETERS, P(I), SUBSTITUTED C INTO THE SPIN-HAMILTONIAN, THE TRIAL PARAMETERS C ARE EXPRESSED IN GAUSS AND THE ANGLES IN RADIANS. C THE CALCULATED FIELDS ARE IN GAUSS.	
SUBROUTINE HNTRIG(P,NANGLF,THETA,PHI,DPPH,H) DIMENSION P(7),H(5,5,6),DPPH(5),ALPHA(5),BETA(5),THETA(5),PHI(5),C 1(5),GX(5),THETAD(5) DO 500 NA=1,NANGLE	2
G(NA) = SORT((P(1)*COS(THETA(NA)))**2+(P(2)*SIN(THETA(NA)))**2) ALPHA(NA)=PHI(NA)	
THETAD(NA)=THETA(NA)*180.0/3.141593 IF (ABS(THETAD(NA)-90.0)-0.2) 5C1,5C1,502 501 BETA(NA)=THETA(NA)	
$\frac{60 \text{ TO } 503}{502 \text{ BETA(NA)=ATAN(P(2)*TAN(THETA(NA))/P(1))}$	-
GX (NA) = GE / G(NA) $CB = COS (BETA(NA))$	
SB=SIN(BFTA(NA)) $CA=COS(ALPHA(NA))$ $SA=SIN(ALPHA(NA))$	
CA3=COS(3.*ALPHA(NA)) SA3=STN(3.*ALPHA(NA)) A20=P(6)*(3.*CP**2=1.)(2	
A20=9(3)*(3.*CD**2=1.)/2. A21=-3.*P(5)*SIN(2.*BETA(NA)) A22=3.*P(5)*SB**2/2.	
A40=(P(6)*(35.*CB**4+30.*CB**2+3.)+P(7)*SB**3*CB*CA3)/8. . A41RE=(20.*P(6)*SB*CB*(37.*CB**2)+P(7)*SB**2*(4.*CP**2-1.)*CA3)/ 14.	,
A41IM=3.*P(7)*SB**2*CB*SA3/4. A41AP=A41RE**2+A411M**2	
A42RE=(10.*P(6)*SB**2*(7.*CB**2-1.)+P(7)*(2.*SB*CB**3*CA3))/4. A421M=P(7)*(SB*(3.*CB**2-1.)*SA3)/4. A42AB=A42RE**2+A42IM**2	-,
A43RE=(-140.*P(6)*SB**3*CB+P(7)*(4.*CB**4+3.*CB**2+3.)*CA3)/4. A43IM=P(7)*CB*(59.*CB**2)*SA3/4. A43AB=A43RF**2+A43[#**2	
A44RF=(35.*P(6)*SP**4+P(7)*(-SB*CB*(3.+CP**2)*CA3))/8. A44IM=P(7)*SP*(CP**2+1.)*SA3/8. A44AB=A44FF**2+A44IM**2	
$CK = -SQRT((P(3)*CR)**2+(P(4)*SB)**2)$ $HO = DP P H(NA)*1 \cdot 0006493$ $P = A P + (NA)*1 \cdot 0006493$	
A212=A21**2 A222=A22**2	
SB2=SIN(2.*BETA(NA)) P2A22=B2A2**2	

	AB2=(P(4)*P(3)/CK)**2
	D0.500  MN=1.6
	X = MN
	XN=(72.*X1)/2.
	XN2=XN**2
	H(NA,1,MN)=(HO-4.*(A2O+A4O)+CK*XN+(8.*A212/94.*A222/9A41A8/40.
	1+A42A6/20.+A43A8/120.+A21*A41RE+A22*A42RE+2.*(A21+A41RE)*XN*B2A2*S
	2B2+(35./4XN2)*(AB2+P(4)**2)/4.+XN2*B2A22*SB2**2/2.+2.*XN*P(3)*P(
	34)**2/CK)/HO)*CX(NA)
	H(NA, 5, MN) = (H0+4.*(A2C+A40)-CK*XN-(R.*A212/94.*A222/9A41A3/40.
	1+A42AB/20.+A43AB/120.+A21*A41RE+A22*A42RE-2.*(A21+A41RE)*XN*B2A2*S
	282+(35-/4XN2)*(AB2+P(4)**2)/4-+XN2*B2A22*SB2**2/2-2-*XN*P(3)*P(
	34)**2/CK)/HD)*GX(NA)
	H{NA,2,MN}=(HO-(2.*A2O-5.*A4O)-CK*XN-(-A2]2/9.+5.*A222/9.+A41AB/5.
	1+9.*A42AB/80A43AB/120.+A44AB/20A21*A41PE+A22*A42RE/2.+(A21-5.*
	2A41RE/2.)*XN*B2A2*SB2+(35./4XN2)*(AE2+P(4)**2)/4.+XN2*B2A22*SB2*
	3*2/2.+XN*P(3)*P(4)**2/CK)/H0)*GX(NA)
	H{NA,4,MN}=(H0+(2.*\20-5.*A40)-CK*XN-(-A212/9.+5.*A222/9.+A41AB/5.
	1+9.*^42AB/80^43A8/120.+A4448/20A21*A418E+A22*A42RE/2(A21-5.*
	2A41RE/2.)*XN*B2A2*SB2+(35./4XN2)*(AB2+P(4)**2)/4.+XN2*B2A22*SB2*
	3*2/2XN*P(3)*P(4)**2/CK)/HP)*GX(NA)
500	H(NA,3,MN)=(HO-CK*XN-(-4.*A212/9.+8.*A222/9A41AR/4A42AB/10.+A4
	13AB/60.+2.*A21*A41RE/32.*A22*A42AB+(35./4XN2)*(AB2+P(4)**2)/4.
	2+XN2*B2A22*SB2**2/2.)/H0)*GX(NA)
	RETURN
	END

## SUBFOUTINE LLSQ

PURPESE TO SO THE E WITH LINEA	LVE LINEAR LEAST SQUARES PROBLEMS, I.E. TO MINIMIZE UCLIDEAN NORM OF B-A*X, WHERE A IS A M BY N MATPIX M NOT LESS THAN N. IN THE SPECIAL CASE M=N SYSTEMS OF R EQUATIONS MAY BE SOLVED.
USAGE	
CALL	LLSQ (A, B, M, N, L, X, IPIV, EPS, IEP, AUX)
DESCRIPT	ION OF PARAMETERS
Λ	- M BY N COEFFICIENT MATRIX (DESTROYED).
В	- M BY L RIGHT HAND SIDE MATRIX (DESTROYED).
М	- ROW NUMBER OF MATRICES A AND B.
N	- COLUMN NUMBER OF MATRIX A, ROW NUMBER OF MATRIX X.
1	- COLUMN NUMBER OF MATRICES B AND X.
X	- N BY I SCLUTION MATRIX.
IPIV	- INTEGER OUTPUT VECTOR OF DIMENSION N WHICH
	CONTAINS INFORMATIONS ON COLUMN INTERCHANGES
	IN MATRIX A. (SEE REMARK NO.3).
E P S	- INPUT PARAMETER WHICH SPECIFIES A RELATIVE
	TOLERANCE FOR DETERMINATION OF RANK OF MATRIX A.
IER	- A RESULTING ERROF PARAMETER.
AUX	- AUXILIARY STOPAGE ARRAY OF DIMENSION MAX(2*N.L).
	ON RETURN FIRST & LOCATIONS OF AUX CONTAIN THE
an a	RESULTING LEAST SQUARES.
REMARKS	

(1) NO ACTION BESIDES ERROR MESSAGE IER=+2 IN CASE M LESS THAN N.

- (2) NO ACTION BESIDES ERROR MESSAGE IER=-1 IN CASE OF A ZERO-MATRIX A.
  - (3) IF RANK K OF MATRIX A IS FOUND TO BE LESS THAN N BUT GREATER THAN O, THE PROCEDURE PETURNS WITH ERROR CODE IER=K INTO CALLING PROGRAM. THE LAST N-K ELEMENTS OF VECTOR IPIV DENOTE THE USELESS COLUMNS IN MATRIX A. THE REMAINING USEFUL COLUMNS FORM A BASE OF MATRIX A.
- (4) IF THE PROCEDURE WAS SUCCESSFUL, ERROR PARAMETER IER IS SET TO 0.

SUPROUTINES AND FUNCTION SUBPROGRAMS REQUIRED NONE

METHOD

HOUSEHOLDER TRANSFORMATIONS ARE USED TO TRANSFORM MATRIX A TO UPPER TRIANGULAR FORM. AFTER HAVING APPLIED THE SAME TRANSFORMATION TO THE RIGHT HAND SIDE MATRIX B, AN APPROXIMATE SOLUTION OF THE PROBLEM IS COMPUTED BY BACK SUBSTITUTION. FOR DEFERENCE, SEE G. GOLUB, MUMFRICAL METHODS FOR SOLVING LINEAR LEAST SQUARES PROPLEMS, NUMERISCHE MATHEMATIK, VOL.7, ISS.3 (1965), PP.206-216.

	$DIMENSION \ A(1), B(1), X(1), IPIV(1), AUX(1)$
	ERROR TEST
	IF(M-N130,1,1
	GENERATION OF INITIAL VECTOP S(K) (K=1,2,,N) IN STORAGE
	LOCATIONS AUX(K) $(K=1,2,\ldots,N)$
1	PIV=0.
	TEND=0
	DO 4 K=1, N
	IPIV(K) = K
2	
Ľ.	
	1 = 1 + 2 + 1 + 4 + 3
3	PIV=4
	KPIV=K
4	CONTINUE
	FREDRITEST
	IF(PIV)31,31,5
	DEFINE TOLERANCE FOR CHECKING RANK OF A
5	SIG = SQRT(PIV)
	TOL=SIG*ABS(EPS)
	DECOMPOSITION LOOP
	DU 21 K=1,N
	INTERCHANGE K-TH COLUMN OF A WITH KPIV-TH IN CASE KPIV.GT:
6	H=AIJX(K)
	AUX(K) = AUX(KPIV)
	AUX(KPIV)=H
	[D=]*N
	DO 7 I=IST, IEND
	J=1+[[]
	$H = \Delta (I)$
	$\Delta(J) = \Delta(J)$

8 IF(K-1)11,11,9 9 SIG=0.DO 10 I=IST, IEND 10 SIG=SIG+A(I)\*A(I)SIG=SOBT(SIG)С TEST ON SINGULARITY С IF(SIG-TOL)32,32,11 С Č GENERATE CORRECT SIGN OF PARAMETER SIG 11 H=A(IST)1F(H)12,13,13 12 SIG = -SIGС SAVE INTERCHANGE INFORMATION С 13 IPIV(KPIV) = IPIV(K)IDIA(K)=KDIA C GENERATION OF VECTOR UK IN K-TH COLUMN OF MATRIX A AND OF С PAPAMETER BETA C BETA=H+SIG A(IST) = BETABETA=1./(SIG\*BETA) J=N+KAUX(J) = -SIGIF(K-N)14,19,19 Ċ C TRANSFORMATION OF MATRIX A 14 PIV=0. ID=0 JST = K + 1KPIV=JST DO 18 J=JST,NID=ID+M11=0. 00 15 I=IST, IEND II=I+ID15 H=H+A(I)\*A(II) H=BETA\*H DO 16 I=IST, IEND II = I + ID16  $\Lambda(II) = \Lambda(II) - \Lambda(I) * H$ С UPDATING OF ELEMENT S(J) STORED IN LOCATION AUX(J) Ċ 11=1ST+1DH = A(IX(J) - A(II) \* A(II) $\Delta U \times (J) = H$ IF(H-PIV)18,18,17 17 PTV=H KPIV=J**18 CONTINUE** 

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C		
С		TRANSFORMATION OF RIGHT HAND SIDE MATRIX B
	19	00 21 J=K,LM,M
	-	H=0.
		DD 20 I=J, HND
		$H=H+A(II) \times B(I)$
	20	I I = I I + 1
		H=BETA*H
, i		
		$B(1) = B(1) = A(11) \neq H$
÷	21	
С		END OF DECOMPOSITION LOOP
C		BACK SUBSTITUTION AND BACK INTERCHANGE
		$I \in \mathbb{R} = 0$
		1 = N
		1 M=1 *N
		$D(Y) = 1 - (A(Y)/2 \pm N)$
	~ .	→ X ( K ) = P 1 V % B ( 1 )
	2.2	
		IF(N-1)26, 26, 23
	23	UST=(1)+1+1+1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1
		DO 25 J=2.N
		1ST = 1ST - M - 1
		k = N + N + 1 - 1
		$DT_{1+1} = I = 0$
		$F \downarrow V = \downarrow \bullet / P \cup A \setminus B$
;		
		1D = 1P I V (KS) I - KSI
1		IST = 2 - J
		D0 25 K=1,L
		H=B(KST)
		1ST=1ST+1
		IEND = IST + J - 2
		TT=1ST
		00 24 1±1ST. LEND
		T = T + M
	21	
	. 74	
		1I=1+10
		X(I) = X(II)
		X(II)=bIA#H
	-25	KST = KST + M
C.		
Ċ		الم
č		COMPUTATION OF LEAST SOURCES
~	26	ISTENA1
	C. 11	
		NU ZY JELYL
		IEND=IEND+M

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		H=0.
	27	DO 28 I=IST, IEND
*	28	$H = H + B(J) \times B(J)$
	29	AUX ( J ) = H
r		RETURN
c		ERROP RETURN IN CASE M LESS THAN N
	30	IER=-2 RETHRN
С		
Ċ	21	FRROR RETURN IN CASE OF ZERO-MATRIX A
	.91	FETURN
C.		ERROR DETHRN IN CASE OF RANK PE MATRIX & LESS THAN N .
U .	32	IFREKAL
		END

## APPENDIX D

Comparison Between Parameters at X-Band and at K-Band

Parameters	K-Band Parameters (G,)	X-Band Parameters (G.)		
	ł	Parameters Cal- culated using Pieczonka's resonant fields in our routine	Pieczonka's published parameters *	
Room 7	emperature	-		
g	$2.0011 \pm 0.0005$	$2.0000 \pm 0.0005$	$2.0001 \pm 0.0005$	
g	2.0010 + 0.005	2.0005 <u>+</u> 0.0005	$2.0005 \pm 0.0005$	
А	-90.74 <u>+</u> 0.25	-91.78 ± 0.25	-91.4 ± 0.4	
В	-89.69 <u>+</u> 0.25	-89.98 ± 0.25	-90.6 <u>+</u> 0.6	
b <sub>2</sub> o	- 5.85 <u>+</u> 0.50	- 6.98 <u>+</u> 0.50	- 7.20 <u>+</u> 0.25	
b <sub>4</sub> °	- 4.31 <u>+</u> 0.50	- 3.39 <u>+</u> 0.50	- 3.60 <u>+</u> 0.15	
Liquid	I Nitrogen Temperatui	re		
s <sub>  </sub>	2.0011 <u>+</u> 0.0005		$2.0007 \pm 0.0010$	
g	2.0010 <u>+</u> 0.0005		2.0020 + 0.0010	
A	-92.22 <u>+</u> 0.25		-91.6 ± 1.0	
В	-90.18 <u>+</u> 0.25	×	-90.6 <u>+</u> 0.6	
b <sub>2</sub> °	-13.39 + 0.50		<b>-</b> 13.7 <u>+</u> 0.25	
<sup>ь</sup> 4	- 3.74 <u>+</u> 0.50	. 1	- 4.2 ± 0.1	

- Spin-Hamiltonian used Eq. II.25
- \* Spin-Hamiltonian used Eq. II.24
- ☑ Calculations were not carried out due to lack of published resonant fields at X-band.

## VITA AUCTORIS

I was born in Hamilton, Ontario, Canada, on June 20, 1943. I graduated from Memorial Public School, Saltfleet, in 1957, and Waterdown Distric High School in 1962. In 1967 I received a B.Sc. from McMaster University, Hamilton, Ontario, where I studied undergraduate physics. In the summer of 1968 I completed secondary school teacher training at the Ontario College of Education, Toronto.

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