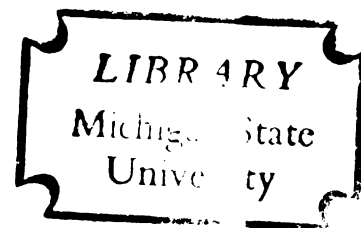


NUCLEAR MAGNETIC RESONANCE STUDY OF
ANTIFERROMAGNETIC $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
JOHN ADDIS CASEY
1967



This is to certify that the

thesis entitled

NUCLEAR MAGNETIC RESONANCE STUDY OF
ANTIFERROMAGNETIC $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$

presented by

John Addis Casey

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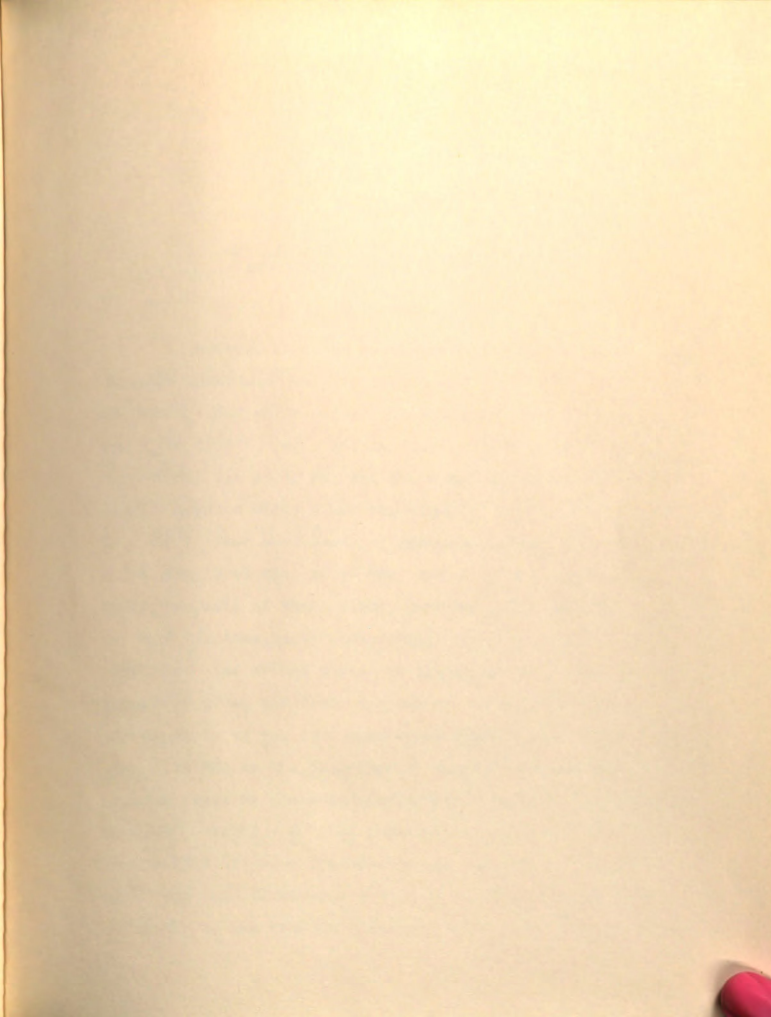
PhD degree in Physics

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Date May 15, 1967

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ABSTRACT

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Proton, chlorine and rubidium nuclear magnetic resonance (NMR) have been studied in triclinic crystals of $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ which become antiferromagnetically ordered at $T_N = 2.24^\circ\text{K}$. At 1.1°K two proton lines were found at 18.96 MHz and 18.50 MHz and their angular dependence in a small applied field fixes the magnetic spin group as 7_1 . Six Cl^{35} lines were found at frequencies 8.25 MHz, 7.79 MHz, 8.56 MHz, 9.63 MHz, 10.48 MHz, and 10.77 MHz. These constitute two sets of three lines, each set corresponding to one of the two chemically inequivalent chlorine sites in the lattice. The second moment of the Mn²⁺ ions was used to properly group the lines subject in the paramagnetic state and extrapolate to the pure quadrupole frequencies of 5.33 MHz and 5.34 MHz in the paramagnetic state. The paramagnetic resonance spectrum contained lines due to Rb^{85} with $I = \frac{5}{2}$ and Rb^{87} with $I = \frac{5}{2}$. Two quadrupole frequencies of 3.229 MHz and 3.229 MHz were observed in the paramagnetic state for Rb^{85} and four lines at 2.38 MHz, 2.78 MHz, 3.18 MHz, and 3.79 MHz in the ordered state at 1.1°K . The Rb^{85} quadrupole

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Proton, chlorine and rubidium nuclear magnetic resonance (NMR) have been studied in triclinic crystals of $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ which become antiferromagnetically ordered at $T_N = 2.24^\circ\text{K}$. At 1.1°K two proton lines were found at 18.96 MHz and 18.30 MHz and their angular dependence in a small applied field fixes the magnetic space group as $\text{P}_s\bar{1}$. Six Cl^{35} lines were found at frequencies 6.25 MHz, 7.72 MHz, 8.56 MHz, 9.63 MHz, 10.48 MHz, and 10.72 MHz. These constitute two sets of three lines, each set corresponding to one of the two chemically inequivalent chlorine sites in the lattice. The second moment of the Hamiltonian was used to properly group the lines subject to the condition that it extrapolate to the pure quadrupole frequencies of 3.85 MHz and 5.34 MHz in the paramagnetic state. The rubidium resonance spectrum contained lines due to both Rb^{87} with $I = \frac{3}{2}$ and Rb^{85} with $I = \frac{5}{2}$. Two quadrupole lines at 2.6743 MHz and 3.2229 MHz were observed in the paramagnetic state for Rb^{85} and four lines at 2.38 MHz, 2.78 MHz, 3.20 MHz, and 3.79 MHz in the ordered state at 1.1°K . The Rb^{87} quadrupole

John Addis Casey

resonance was found at 3.1161 MHz and six lines were observed at 1.22 MHz, 3.89 MHz, 4.18 MHz, 5.12 MHz, 5.42 MHz, and 9.26 MHz at 1.1°K.

The angular variation of the resonance lines in the presence of a small external field was analyzed using the second moment of the Hamiltonian to determine the direction of the internal fields at the chlorine and rubidium sites.

The chlorine internal fields are nearly parallel and with this taken as the direction of magnetization, computer programs were used to calculate the magnitude and direction of internal fields at the various nuclei. The internal fields were calculated for each of the magnetic lattices allowed by magnetic space group P_5^1 and compared with the measured fields.

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By

John Addis Casey

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics

1967

ACKNOWLEDGMENTS

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LIST OF FIGURES

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor R. D. Spence for his assistance and support in this work, to Dr. V. H. ... efforts during the collection and ... and to Dr. J. A. Cowen, Dr. ... and Dr. E. H. Carlson for their ... this thesis.

- 1. ...
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The author wishes to express his gratitude to Professor R. D. Spence for his continuing guidance and support in this work, to Dr. V. Nagarajan for his diligent efforts during the collection and reduction of the data and to Dr. J. A. Cowen, Dr. H. Forstat, Dr. P. M. Parker, and Dr. E. H. Carlson for their assistance in preparing this thesis.

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- B. Crystal Structure

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- A. Proton Resonance
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- D. Internal Fields
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I. INTRODUCTION

This section discusses in general terms some of the information about antiferromagnetic materials obtainable with nuclear magnetic resonance. $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ is among those hydrated transition metal salts which are of interest partly because proton magnetic resonance is easy to interpret when applied to the investigation of ordered states. Protons are ideal probes of the magnetic fields in the crystal because they are not effected by a quadrupole interaction and so respond only to the local field.

The transition temperature can be measured by observing the abrupt change in the resonance lines as the temperature is changed through the transition. Pure quadrupole resonance is ideal for this purpose, because at the transition the quadrupole energy levels are split by the appearance of an internal field and the resonance will suddenly disappear to reappear at other frequencies. Ordered state resonances are usually unsatisfactory for this purpose because the lines weaken and disappear at a temperature somewhat below T_N . Proton magnetic resonance in the paramagnetic state can be used for this measurement, but the applied field may shift the transition temperature.

Perhaps the most precise measurement that can be made with NMR is the temperature dependence of the sublattice

magnetization. Since resonance can be done without an external field, the nuclei respond to the local internal field which is a direct measure of the magnetization. For most nuclei the effects of the quadrupole interaction have to be considered in deducing the magnetization from the resonance spectrum, but the proton frequencies are directly proportional to the magnetization. The direction of the internal field at nuclei located within the distribution of magnetization about the magnetic ions is a good approximation to the direction of magnetization. Even a weak transferred hyperfine interaction produces fields at these nuclei much larger than the dipole fields so that the internal field at such a nucleus is nearly parallel to the spin of its neighboring magnetic ion.

The distribution of internal fields and the magnetic spin arrangement are determined by the crystal's magnetic space group. The number of possible magnetic space groups is restricted by the symmetry of the magnitudes and directions of the internal fields. If the atomic coordinates are known, calculation of the local fields predicted by each possibility may select the correct space group.

Combination of the crystal structure and NMR data may suggest possible exchange paths in the crystal. For example an atom situated between two magnetic atoms and subject to a particularly large hyperfine field is almost certainly a link in a super-exchange path.

Finally NMR can be used to map a crystal's magnetic phase diagram by observing the antiferromagnetic to spin-flop and spin-flop to paramagnetic transitions as functions of the temperature and externally applied field. At the spin-flop transition the magnetic spins align themselves normal to the applied field; the size of the field required to produce this effect is a measure of the anisotropy energy holding the spins along the magnetization direction.

The Hamiltonian composed of Zeeman and electric quadrupole interactions.

$$H = -\vec{\mu} \cdot \vec{H} + Q: \nabla \vec{E} \quad (1)$$

where $\vec{\mu}$ is the nuclear magnetic moment, $\vec{H}$ the magnetic field at the nuclear site, Q the nuclear quadrupole moment tensor, and $\nabla \vec{E}$ is the electric field gradient tensor. In general two very different effects contribute to $\vec{H}$: the dipolar field due to the magnetic ions throughout the lattice, and the transferred hyperfine interaction. The magnitude and direction of the dipolar field depends on the position of the nucleus with respect to the magnetic ions in a rather classical way while the transferred hyperfine interaction arises from the exclusion principle.

Insofar as their configuration they are identical except the free ion wave functions of the Mn^{2+} ion and the Mn^{2+} ion are non-orthogonal. In addition the configuration required by the exclusion principle for the Mn^{2+} ion and the Cl^- electrons whose spin are parallel to the Mn^{2+} spin.

II. THEORY

A. The Hamiltonian

The nuclear magnetic resonance spectrum for the nuclei studied in $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ is determined by a Hamiltonian composed of Zeeman and electric quadrupole interactions.

B. The Method of Moments

$$H = -\vec{\mu} \cdot \vec{H} + Q:\nabla\vec{E} \quad (1)$$

where $\vec{\mu}$ is the nuclear magnetic moment, $\vec{H}$ the magnetic field at the nuclear site, Q the nuclear quadrupole moment tensor, and $\nabla\vec{E}$ is the electric field gradient tensor. In general two very different effects contribute to $\vec{H}$, the dipolar field due to the magnetic ions throughout the lattice, and the transferred hyperfine interaction. The magnitude and direction of the dipolar field depends on the position of the nucleus with respect to the magnetic ions in a purely classical way while the transferred hyperfine interaction arises from the exclusion principle.

Insofar as their configuration and spin spaces overlap the free ion wave functions of the electrons of the Cl^- and Mn^{++} ion are non-orthogonal. To achieve the orthogonality required by the exclusion principle the wave functions of Cl^- electrons whose spins are parallel to the d electrons

of the Mn^{++} must contract towards the chlorine nucleus. The wave functions of Cl^- electrons whose spins are anti-parallel to the d electrons of Mn^{++} mix with those of the d electrons to form covalent bonds with the result that their density at the chlorine nucleus is reduced. The enhancement of parallel spin density and the reduction of anti-parallel spin density in the neighborhood of the chlorine gives rise to the hyperfine interaction.

B. The Method of Moments

The energy levels of the Hamiltonian depend in a complicated way on various parameters. However analysis of the resonance spectrum can be greatly simplified by recourse to the moments of the Hamiltonian. The m^{th} moment is defined:

$$\Gamma_m = \text{trace } (H^m) \quad (2)$$

Brown and Parker¹ express the Γ_m in terms of m^{th} degree polynomials in the resonance frequencies, but they can also be expressed in terms of m^{th} degree scalars involving $\vec{H}$ and $\nabla \vec{E}$ as follows:

$$\Gamma_2 = f_2 \vec{H} \cdot \vec{H} + g_2 \nabla \vec{E} \cdot \nabla \vec{E} \quad (3)$$

$$\Gamma_3 = f_3 \vec{H} \vec{H} : \nabla \vec{E} + g_3 (\nabla \vec{E} \cdot \nabla \vec{E}) : \nabla \vec{E} \quad (4)$$

Since the Hamiltonian is traceless, $\Gamma_1 = 0$. The coefficients involve only functions of the nuclear spin and the coupling constants $a = \frac{\gamma}{2\pi}$ and $b = \frac{eQ}{2h}$ and are evaluated by comparison with Brown and Parker as shown in Table I.

Table I. Coefficients* for Calculating the Γ_m

Coefficient	$I = \frac{3}{2}$	$I = \frac{5}{2}$
f_2	$5a^2$	$\frac{35}{2}a^2$
g_2	$\frac{2}{3}b^2$	$\frac{14}{25}b^2$
f_3	$6a^2b$	$\frac{84}{5}a^2b$
g_3	0	$\frac{4}{25}b^3$

*Values are in frequency units

If $\nu_1, \nu_2, \dots, \nu_{2I}$ are the frequencies of transitions between adjacent energy levels, then:

$$\Gamma_2 = \frac{1}{(2I+1)^2} \sum_{n=0}^{2I} \sum_{i=1}^{2I} \sum_{j=1}^{2I} C_i(n) C_j(n) \nu_i \nu_j \quad (5)$$

$$\Gamma_3 = \frac{1}{(2I+1)^3} \sum_{n=0}^{2I} \sum_{i=1}^{2I} \sum_{j=1}^{2I} \sum_{k=1}^{2I} C_i(n) C_j(n) C_k(n) \nu_i \nu_j \nu_k \quad (6)$$

where

$$C_k(n) = k \quad ; \quad k \leq n$$

$$C_k(n) = k - (2I - 1) \quad ; \quad k > n$$

In the paramagnetic state $\tilde{H} = 0$ and, representing the pure quadrupole frequencies for $I = \frac{5}{2}$ as ν_I and ν_{II} and for $I = \frac{3}{2}$ as ν_Q :

$$\Gamma_2^P = v_Q^2 = \left(\frac{eQq}{2h} \right)^2 \left(1 + \frac{\eta^2}{3} \right) \quad ; \quad I = \frac{3}{2} \quad (7)$$

$$\Gamma_2^P = \frac{4}{3} \left(v_I^2 + v_I v_{II} + v_{II}^2 \right) = \frac{21}{25} \left(\frac{eQq}{2h} \right)^2 \left(1 + \frac{\eta^2}{3} \right) \quad ; \quad I = \frac{5}{2} \quad (8)$$

$$\Gamma_3^P = 0 \quad ; \quad I = \frac{3}{2} \quad (9)$$

$$\Gamma_3^P = \frac{2}{9} \left(2v_I^3 + 3v_{II}v_I^2 - 3v_{II}^2v_I - 2v_{II}^3 \right) = \frac{4}{25} \left(\frac{eQq}{2h} \right)^3 (1 - \eta^2) \quad ; \quad I = \frac{5}{2} \quad (10)$$

where

$$\eta = \frac{\frac{\partial E_z}{\partial z}}{\frac{\partial E_x}{\partial x} - \frac{\partial E_y}{\partial y}}$$

and

In the antiferromagnetic state for $I = \frac{3}{2}$ equations (3) and (5) combine to yield:

$$\begin{aligned} \Gamma_2^a &= \frac{3}{4}v_1^2 + v_2^2 + \frac{3}{4}v_3^2 + v_1v_2 + \frac{1}{2}v_1v_3 + v_2v_3 \\ &= 5 \left(\frac{\gamma}{2\pi} \right)^2 H^2 + \left(\frac{eQq}{2h} \right)^2 \left(1 + \frac{\eta^2}{3} \right) \end{aligned} \quad (11)$$

The magnitude of the internal field is found from equations (7) and (11)

$$H^2 = \frac{1}{5} \left(\frac{2\pi}{\gamma} \right)^2 \left(\Gamma_2^a - \Gamma_2^P \right) \quad ; \quad I = \frac{3}{2} \quad (12)$$

In order to find the direction of the internal field, a small external field is applied $\delta \vec{H} \ll \vec{H}$. The resulting change in the second moment is:

$$\delta\Gamma_2^a = \nabla_H \Gamma_2^a \cdot \delta\vec{H} \quad (13)$$

From equation (11):

$$\delta\Gamma_2^a = 10 \left(\frac{\gamma}{2\pi} \right)^2 \vec{H} \cdot \delta\vec{H}$$

Combining equations (5), (13), and (14) and writing $\vec{H} = H\vec{\xi}_1$

$$\vec{\xi}_1 = \frac{1}{80H} \left(\frac{2\pi}{\gamma} \right)^2 \sum_{n=0}^3 \sum_{i=1}^3 \sum_{j=1}^3 C_i(n) C_j(n) v_i \nabla_H v_j ; I = \frac{3}{2} \quad (15)$$

Writing $\nabla_H v_j = K_j \vec{a}_j$ where $\vec{a}_j$ is a unit vector in the direction along which $\delta\vec{H}$ must be applied to produce the largest shift in v_j and where K_j is the magnitude of this shift then:

$$\vec{\xi}_1 = \sum_{j=1}^3 A_j \vec{a}_j \quad (16)$$

where, because the resonance patterns exhibit three-fold

$$A_j = \frac{1}{80H} \left(\frac{2\pi}{\gamma} \right)^2 \sum_{n=0}^3 \sum_{i=1}^3 C_i(n) C_j(n) v_i K_j \quad (17)$$

Thus the direction of the internal field at a nucleus with spin $I = \frac{3}{2}$ can be expressed as the sum of three vectors. The magnitude and direction of each vector is determined by the maximum shift of one of the lines in the resonance spectrum and the direction along which the external field must be applied to produce this shift.

C. The Magnetic Space Group

The NMR spectrum with and without an externally applied field provides information about the symmetry elements which govern the arrangement of magnetic moments and the disposition of magnetic fields throughout the crystal. The zero field spectrum of a particular nucleus gives the number of local fields of different magnitude at the sites of that nucleus, and the applied field spectrum can distinguish local fields of the same magnitude and different directions.

The process of determining the space group which describes the magnetic symmetry of the crystal consists in selecting those groups whose elements leave the NMR spectra invariant. In general there will be more than one such group, because the resonance patterns cannot distinguish symmetry elements involving translation from the corresponding elements without translation. That is, the resonance spectra reflect only the magnetic point group.

If the crystal structure and direction of magnetization are known it is possible to select from among the remaining possible space groups that group for which a calculation of the internal fields yields best agreement with the experimental measurements. If $\vec{r}$ is the vector from a particular nucleus to the i^{th} magnetic ion whose moment is $\vec{\mu}_i$ and I is the unit dyad, the dipolar field at the nucleus is:

$$\vec{H} = \sum_i \left(\frac{3\vec{r}_i \vec{r}_i}{r_i^5} - \frac{I}{r_i^3} \right) \cdot \vec{\mu}_i \quad (18)$$

The i^{th} magnetic moment is related to any particular moment $\vec{\mu}_0$ by equation (19). If the anisotropy energy is deter-

$$\vec{\mu}_i = \vec{H}_1 \cdot \vec{\mu}_0 \quad (19)$$

The elements of $\vec{H}_1$ are determined by the magnetic space group. The dipolar internal field is:

$$\vec{H} = \sum_i \left(\frac{3\vec{r}_i \vec{r}_i}{r_i^5} - \frac{I}{r_i^3} \right) \cdot \vec{H}_1 \cdot \vec{\mu}_0 \quad (20)$$

For a nucleus such as chlorine the internal field is due predominantly to the transferred hyperfine interaction and so is nearly parallel to the direction of magnetization. Thus the direction of $\vec{\mu}_0$ is approximately the direction of the chlorine internal field. In some crystals of sufficiently high symmetry it may be obvious that the magnetization direction must lie along a particular symmetry axis; however this is not the case in triclinic $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$.

D. Dipolar Anisotropy Energy

The direction of magnetization is determined by the crystalline field of the coordination group about the magnetic ion and by the dipole-dipole interactions among the magnetic ions. In cases where the crystalline field effect

is small then the spins align themselves in such a way as to minimize the energy of the lattice of dipoles. If a magnetic moment $\vec{\mu}_0$ is placed at the origin, then the field at the origin due to all the dipoles $\vec{\mu}_i$ at positions $\vec{r}_i$ is given by equation (20). If the anisotropy energy is determined by such dipole-dipole interactions, then $\vec{\mu}_0$ will align itself parallel to $\vec{H}$, in the following way,

$$A\vec{\mu}_0 = \sum_i \left(\frac{3\vec{r}_i\vec{r}_i}{r_i^5} - \frac{1}{r_i^3} \right) \cdot \vec{H}_1 \cdot \vec{\mu}_0 \quad (21)$$

For a triclinic crystal

$$\vec{H}_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \text{ for } \vec{\mu}_i \text{ parallel to } \vec{\mu}_0$$

$$\vec{H}_1 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}; \text{ for } \vec{\mu}_i \text{ antiparallel to } \vec{\mu}_0$$

It is clear from equation (21) that the direction of magnetization is one of the principle axes of the tensor T:

$$T = \sum_i \left(\frac{3\vec{r}_i\vec{r}_i}{r_i^5} - \frac{1}{r_i^3} \right) \cdot \vec{H}_1 \quad (22)$$

The crystal and coil were mounted on the end of a transmission line consisting of a parallel wire with a center conductor. The transmission line was mounted in a dewar so that the crystal could be cooled by liquid He⁴. By pumping on the dewar the temperature of the crystal could be varied from 4.2°K to 1.2°K.

III. APPARATUS

The NMR data was taken on a Pound-type marginal oscillator spectrometer. Signals of sufficient strength could be displayed directly on the oscilloscope, and weaker signals could be recorded with phase sensitive detection while the oscillator frequency was motor driven. Frequencies were measured by means of a short length of wire placed near the grid circuit in the oscillator whose pickup was amplified and put into an electronic frequency counter.

The oscillator r.f. coil was wound directly on the crystal, the number of turns varying with the working frequency range desired. The tuning capacitor in the oscillator normally provided a frequency range of about 4 MHz. For a given coil, the frequency could be extended downward considerably by the addition of extra capacitance in parallel with the tuning condenser.

The crystal and coil were mounted at the end of a transmission line consisting of a german silver tube with center conductor. The transmission line was run down into a dewar so that the crystal could be immersed directly in liquid He⁴. By pumping on the He⁴ bath the temperature of the crystal could be varied from 4.2 to 1.1 degrees Kelvin.

For the experiments involving angular variations the crystal and coil were mounted on a pulley wheel at the end of the transmission line. A string, attached at one end to a spring inside the top of the dewar, was wrapped around the pulley and connected to a brass rod running out the dewar head through an O-ring seal. By moving the rod up and down the crystal could be rotated. This allowed measurements to be made in two perpendicular planes without removing the crystal from the dewar to remount it in a new orientation.

Zeeman modulation was used in all the experiments described here. The modulation was provided by a pair of Helmholtz coils placed on the outside of the dewar and free to rotate about the axis of the dewar. In the experiments requiring a small external d.c. field, one coil of the pair carried the a.c. modulation current, while the other carried direct current.

The chemical composition of the crystals was checked in this way by sending a portion of the crystal for analysis. Table II compares the calculated composition with the analyst's measurements.

The crystals grew as single crystals, but with no well developed seed faces. The morphology was not ideal but the crystals had insufficient time to develop a well defined twin.

Table II. Calculated and measured percentages

Element	Calculated, percent	Measured percentage
Rubidium	41.3	41.3
Manganese	13.8	13.8
Chlorine	35.1	35.1

IV. SAMPLE PREPARATION

A. Crystal Growth and Chemical Analysis

Solutions were prepared by adding RbCl to a warm saturated solution of MnCl_2 in sufficient amount to saturate it. The solution was allowed to evaporate at room temperature in an open beaker. In twelve to twenty-four hours, seed crystals had formed and were allowed to develop until some of the larger ones could be tied and hung in the solution. Sizable crystals could be grown in a comparatively short time; however well shaped single crystals were difficult to obtain perhaps because the crystals tended to grow too fast.

The chemical composition of the crystals obtained in this way was checked by sending a sample for commercial analysis. Table II compares the calculated percentages with the analyst's measurements.

The crystals grew as elongated four sided prisms with no well developed end faces. Saunders² reported on the morphology but his results are very incomplete because his crystals had insufficient faces and had a tendency to twin.

Table II. Results of Chemical Analysis

Element	Calculated Percentage	Measured Percentage
Rubidium	42.3	42.0
Manganese	13.6	13.9
Chlorine	35.1	34.6
Water	8.9	8.8

B. Crystal Structure

Jensen³ studied the structure of this compound and he found it to be triclinic with space group $P\bar{1}$, the only symmetry elements being inversion centers at each corner of the cell, at the face centers, and at the body center of the cell. He reports the chemical cell dimensions as $a = 5.66 \text{ \AA}$, $b = 6.48 \text{ \AA}$, $c = 7.01 \text{ \AA}$, $\alpha = 66.7^\circ$, $\beta = 87.7^\circ$, and $\gamma = 84.8^\circ$; he also gives the atomic coordinates of all the atoms except hydrogen and lists his calculated and observed structure factors. The oxygen and chlorine atoms lie near the corners of a square with manganese at the center and two oxygens lie above and below the plane of the square. Figure 1 shows the crystal structure projected into a plane normal to the a-axis.

The oxygen atoms lie the proper distance from chlorine atoms on different octahedra to form hydrogen bonds. The hydrogen atoms were assumed to lie along these bonds at a

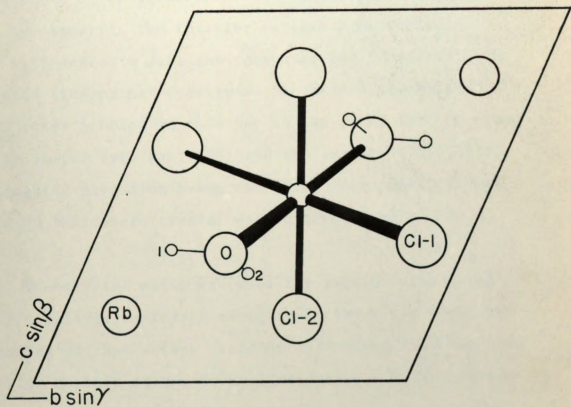


Figure 1.--Structure of $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$

distance of $0.987 \text{ \AA}$ from the oxygen as suggested by El Saffar.⁴

In order to determine the morphology, crystals were mounted on an X-ray diffractometer. Reflections were identified by comparing the relative intensity of various orders with Jensen's data and comparing the 2θ values with calculated interplanar spacings. In the ten crystals of various sizes studied in this way it was found that in every case the larger face was (100) and the smaller (011) with the elongated direction being the $[0\bar{1}1]$ zone axis. It was also found that every crystal was twinned about the $[0\bar{1}1]$ axis.

The crystal which was used for angular measurements was far too large to insert directly in the X-ray beam; it was mounted so that x-rays could be diffracted from one corner. Five corners of the crystal were examined in this way and its orientation was determined from the results. Reflections from four of the corners resulted in identical assignment of axes. These corners all showed very much weaker twin reflections. On the fifth corner, chosen because of its irregular appearance, the reflections from the two kinds of twin material were of nearly equal intensity, making assignment of axes impossible. Apparently the smaller proportion of twinned material became reoriented at some temperature, because at liquid helium temperatures, the angular variations of the resonance lines showed no evidence of twinning.

V. RESULTS AND DISCUSSION

A. Proton Resonance

At 1.1°K two proton resonances were seen in zero applied field. The frequencies of these lines were 18.96 MHz and 18.30 MHz and since $H = \frac{2\pi\nu}{\gamma}$, the magnitudes of the of the internal fields at the proton sites are 4,453 oersted and 4,298 oersted. Figure 2 shows the temperature dependence of the frequency of the two lines and the curve is extrapolated to $T_N = 2.24^\circ\text{K}$.

Figure 3 is the resonance diagram obtained by applying an external field of 82 oersteds in the plane normal to $[0\bar{1}1]$. The diagram shows that the magnetic ordering is antiferromagnetic as each resonance line is split into two lines by the external field. This splitting is a maximum when the applied field is parallel to the projection of the internal field into the rotation plane. Thus the projection of the larger internal field lies at $\phi = 110^\circ$ and the smaller at $\phi = 82^\circ$. Rotation of the field in another plane is then sufficient to determine the direction of the internal fields at the proton sites. The magnitudes and directions of the proton, chlorine, and rubidium fields are summarized in Table VI, which appears in section V-D.

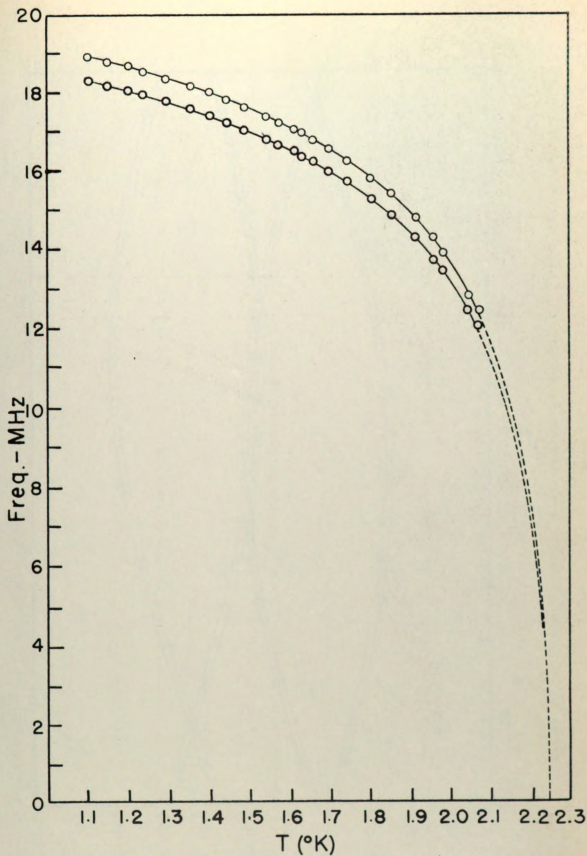


Figure 2.--Temperature Dependence of the Proton Resonance Frequencies

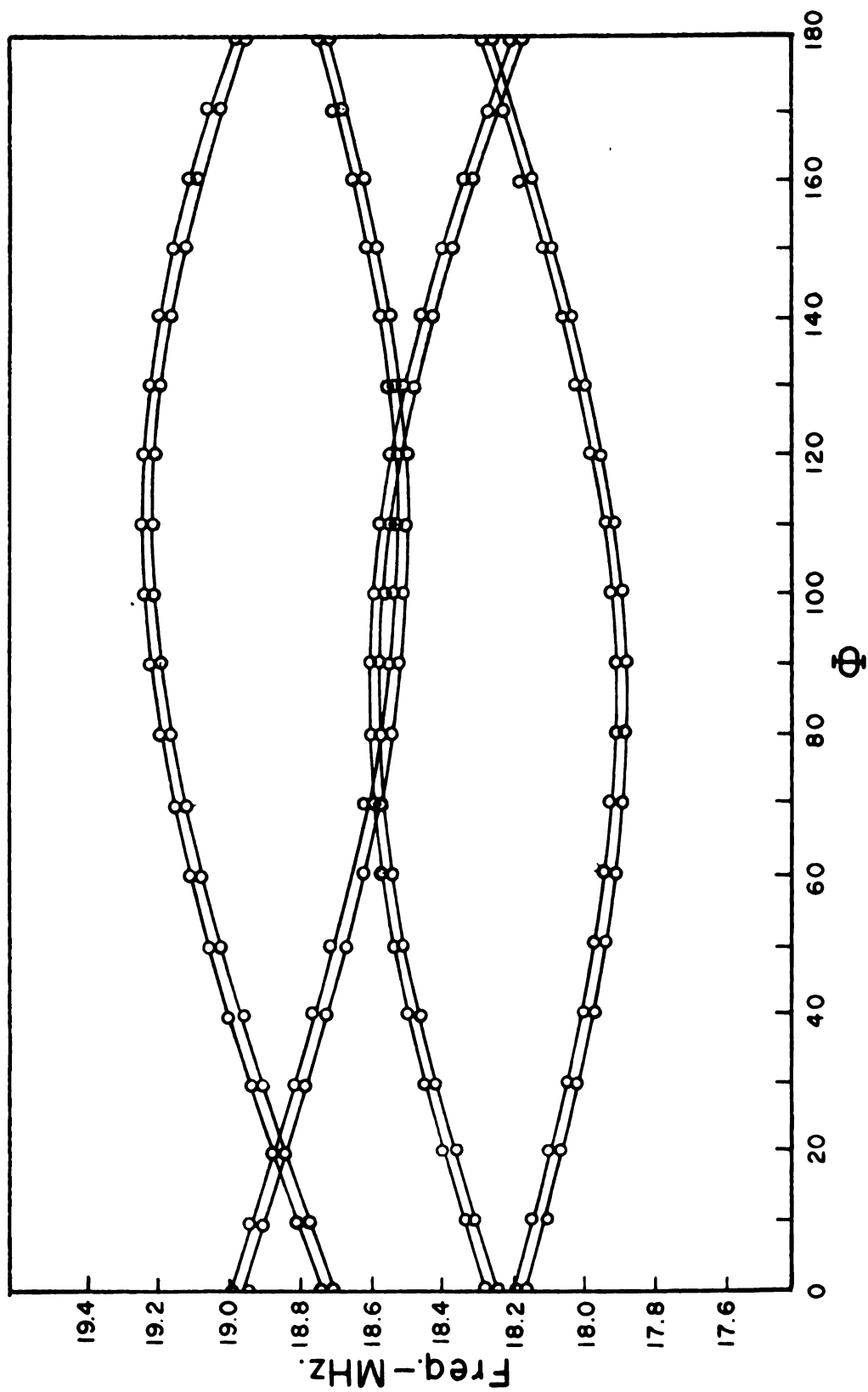


Figure 5. ---Proton Resonance Diagram in an Applied Field of 82 Oersteds

The small splitting of the resonance lines in Figure 3 is due to the dipole-dipole interaction between protons on the same water molecule. That is each proton in a water molecule is effected by the dipolar field of the other proton in the molecule in addition to the much larger fields arising from the magnetic ions. The Hamiltonian for the two protons is:

$$H = -\vec{\mu}_1 \cdot \vec{H}_1 - \vec{\mu}_2 \cdot \vec{H}_2 - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5} + \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} \quad (27)$$

where the subscripts identify the magnetic moments and internal fields at the two proton sites and $\vec{r}$ is the proton-proton vector. The small splitting in Figure 3 arises from the third and fourth terms in the Hamiltonian which were evaluated neglecting very small terms.

$$\Delta\nu = -\frac{g^2 \beta^2}{r^3} (3 \cos \theta_1 \cos \theta_2 - \cos \theta_{12}) \quad (28)$$

where θ_i is the angle between $\vec{H}_i$ and $\vec{r}$ and θ_{12} is the angle between $\vec{H}_1$ and $\vec{H}_2$. The observed splitting is 40.1 kHz for the higher frequency line and 40.4 kHz for the lower while evaluation of $\Delta\nu$ yields 36 kHz. This indicates that the positions assigned the protons are not precisely correct, but this calculation gives no good indication of how they can be corrected.

Figure 3 also shows that the magnetic space group contains only elements which change a given field into an

oppositely directed field. Furthermore it is clear that an anti-inversion center cannot support a non-zero axial vector, since the vector would be transformed by the center into its negative and cancel itself. Thus the sites of the magnetic ions in the lattice cannot be anti-inversion centers.⁵ These two facts lead to the choice of $P_{\bar{1}}$ from among the triclinic groups⁶ as the only possible magnetic space group, but the direction of antitranslation in this group remains to be determined.

B. Chlorine Resonance

In the paramagnetic state two weak Cl^{35} pure quadrupole resonances were observed at 3.853 MHz and 5.335 MHz. In the antiferromagnetic state a total of twelve chlorine resonances were observed. Six of these resonances were strong and six rather weak, arising from Cl^{35} and Cl^{37} respectively. Cl^{37} has somewhat smaller magnetic and quadrupole moments than Cl^{35} and is about one-third as abundant; both isotopes have nuclear spin $I = \frac{3}{2}$. Thus for every strong Cl^{35} resonance there is a weaker Cl^{37} resonance at a lower frequency such that $\nu^{35}/\nu^{37} \sim 1.2$. The Cl^{37} resonance is of little interest beyond identifying the resonant nuclei as chlorine.

At 1.1°K the six Cl^{35} resonances occur at 10.72, 10.48, 9.63, 8.56, 7.72 and 6.25 MHz. Figure 4 shows their temperature dependence and the two pure quadrupole lines

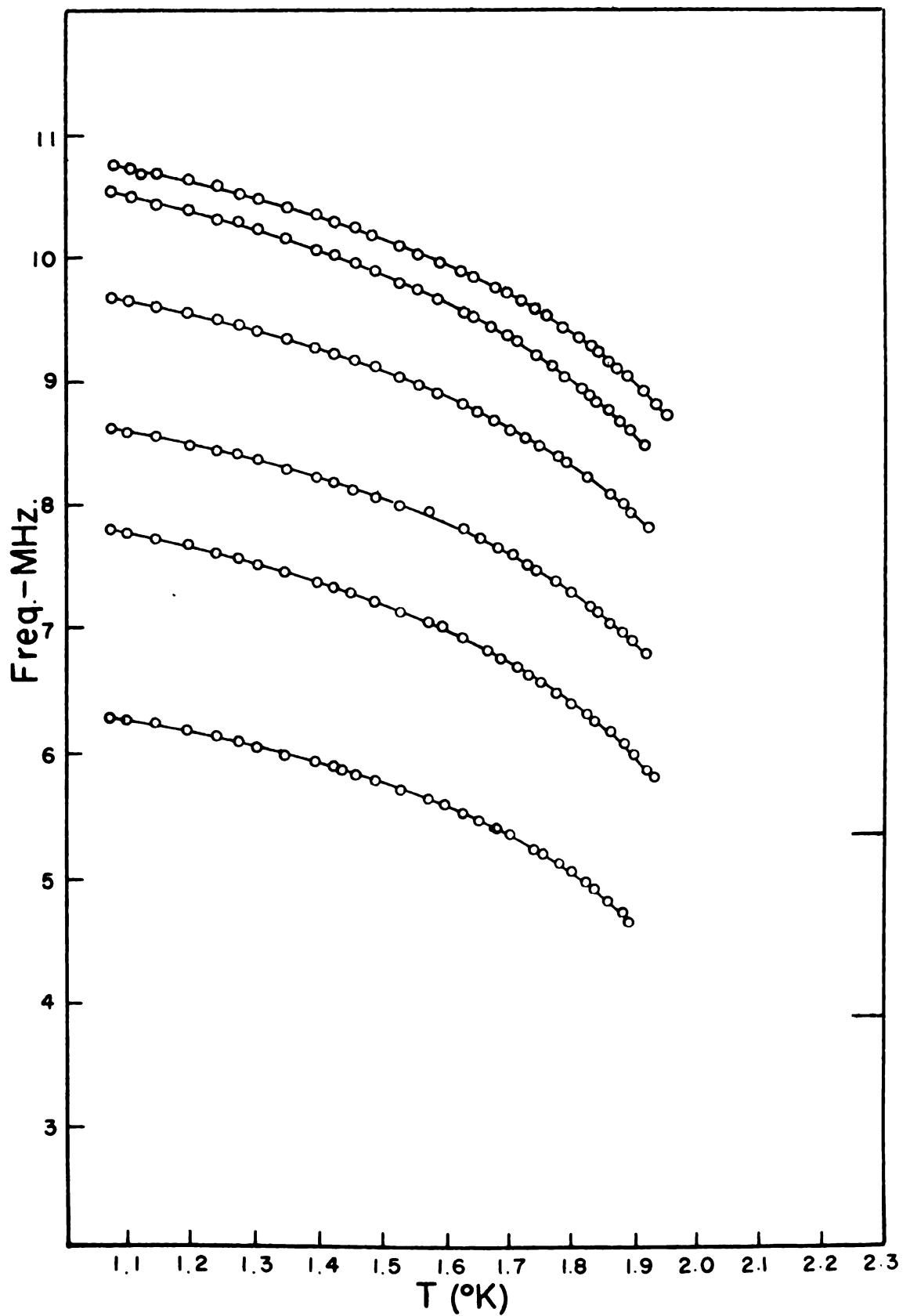


Figure 4.--Temperature Dependence of the Cl^{35} Resonance Frequencies

above T_N . The ordered state lines gradually disappear as the temperature approaches T_N so that the resonances cannot be observed above 1.55°K.

Of the six Cl^{35} resonances, three must be associated with each of the inequivalent chlorine sites in the chemical unit cell. The proper selections were made based on the fact that, when extrapolated into the paramagnetic state, the second moment equals the square of the pure quadrupole frequency.

The internal field at the proton and chlorine sites may be written:

$$\vec{H}_p = \vec{G}_p \langle S \rangle \quad (29)$$

and

$$\vec{H}_{Cl} = \vec{G}_{Cl} \langle S \rangle \quad (30)$$

where $\langle S \rangle$ is the expectation value of the spin of the Mn^{++} ion. The proton field is simply the sum of the dipolar fields of the magnetic ions throughout the lattice while the chlorine field is due principally to the transferred hyperfine interaction with a small contribution from dipolar fields. However $\vec{G}_p$ and $\vec{G}_{Cl}$ are vector functions of the lattice parameters and atomic coordinates and are assumed independent of temperature. Thus

$$H_{Cl}^2 = K H_p^2 \quad (31)$$

and from equation (11) for a temperature T:

$$\Gamma_2(T) = 5K \left(\frac{\gamma C \ell}{\gamma_p} \right)^2 \nu_p^2(T) + \nu_Q^2 \left(1 + \frac{\eta^2}{3} \right) \quad (32)$$

The selection is made by a trial and error choice of three lines from the chlorine spectrum from which Γ_2 is calculated at various temperatures and plotted against the value of $\nu_p^2(T)$ at the same temperatures. If a proper choice of ν_1 , ν_2 , and ν_3 has been made, the graph will be a straight line and can be extrapolated to $\nu_p^2 = 0$ where the intercept will be the square of one of the pure quadrupole frequencies. The results of this process of selection are shown in Table III.

Table III. Assignment of Cl^{35} Lines

Site	Transition*	ν at 1.1-MHz	Calc. ν_Q -MHz	Obs. ν_Q -MHz
A	$(-\frac{3}{2} - - \frac{1}{2})$	10.72		
A	$(-\frac{1}{2} - + \frac{1}{2})$	6.25	3.85	3.85
A	$(+\frac{1}{2} - + \frac{3}{2})$	8.56		
- - - - -				
B	$(-\frac{3}{2} - - \frac{1}{2})$	10.48		
B	$(-\frac{1}{2} - + \frac{1}{2})$	9.63	5.53	5.34
B	$(+\frac{1}{2} - + \frac{3}{2})$	7.72		

*In the high field labeling

The fact that the lines in each set are not approximately equally spaced indicates that the angle between the internal field and the z-axis of the electric field gradient tensor is $\sim 54^\circ$ at which angle equal splitting occurs only at very high fields.

The magnitude of the fields at the two chlorine sites is found from equation (12), and the direction of the fields is found from equation (16) as described in Section II-B. The magnitude and direction of the chlorine fields are listed in Table VI.

C. Rubidium Resonance

Resonance lines were observed for two isotopes of rubidium whose properties are summarized in Table IV. In addition to the fact that Rb^{85} has nuclear spin $I = \frac{5}{2}$ and Rb^{87} has $I = \frac{3}{2}$, the relative quadrupole contribution to the total Hamiltonian is much larger for Rb^{85} than Rb^{87} .

Table IV. Comparison of Rb^{85} and Rb^{87}

Isotope	NMR Frequency MHz/10kG	Abundance %	Spin in $\frac{h}{2\pi}$	Quadrupole Moment $\text{ex}10^{-24} \text{ cm}^2$
Rb^{85}	4.111	72.8	$\frac{5}{2}$	0.28
Rb^{87}	13.932	27.2	$\frac{3}{2}$	0.14

In the paramagnetic state three quadpolar resonances were observed at 3.2229, 3.1161 and 2.6743 MHz. They correspond to the $\pm\frac{5}{2} - \pm\frac{3}{2}$ and $\pm\frac{3}{2} - \pm\frac{1}{2}$ transitions for Rb^{85} and the $\pm\frac{3}{2} - \pm\frac{1}{2}$ transition for Rb^{87} . The ratio of the quadrupole moments of the two isotopes has been reported by Meyer-Berkhout⁷ from beam measurements.

$$R_Q = \frac{Q^{85}}{Q^{87}} = 2.0669 \pm .0005 \quad (36)$$

R_Q can be calculated from equations (7) and (8) in terms of the quadrupole resonance frequencies. Only the assignment of frequencies shown in Table V yields the proper ratio, $R_Q = 2.07 \pm .06$.

Table V. Pure Quadrupole Lines of Rb^{85} and Rb^{87}

Isotope	Spin	Transition	Frequency
Rb^{85}	$\frac{5}{2}$	$\nu_I \quad (\pm\frac{3}{2} - \pm\frac{1}{2})$	$2.6743 \pm .0018$
Rb^{85}	$\frac{5}{2}$	$\nu_{II} \quad (\pm\frac{5}{2} - \pm\frac{3}{2})$	$3.2229 \pm .0060$
Rb^{87}	$\frac{3}{2}$	$\nu_Q \quad (\pm\frac{3}{2} - \pm\frac{1}{2})$	$3.1161 \pm .0016$

An alternate method of selection is based on Cohen's⁸ tables of energy levels as a function of asymmetry parameter, η , for $I = \frac{3}{2}$ and $I = \frac{5}{2}$. Two frequencies can be arbitrarily assigned to the two Rb^{85} transitions and the tables yield a

value for η . Using the ratios of the quadrupole moments and this value of η , the frequency of the Rb^{87} transition can be found from the $I = \frac{3}{2}$ table. The assignment shown in Table V is the only possibility with this internal consistency. The value of the asymmetry parameter obtained is $\eta = 0.78$.

Equations (8) and (10) can also be combined to yield an expression for the asymmetry parameter.

$$\frac{\left(1 + \frac{\eta^2}{3}\right)^3}{\left(1 - \eta^2\right)^2} = \frac{400}{9,261} \frac{(\Gamma_2^P)^3}{(\Gamma_3^P)^2} ; I = \frac{5}{2} \quad (37)$$

With Γ_2^P and Γ_3^P calculated from the frequencies assigned to Rb^{85} this yields $\eta = 0.78$.

In the antiferromagnetic state the Rb^{87} resonance spectrum consists of six lines. The temperature dependence of these lines is shown in Figure 5. Some of the lines could be seen very near the transition temperature so the T_N was measured by watching for the disappearance of the quadrupole lines and the appearance of the ordered state lines as the temperature was slowly lowered. Accurate determination was hampered by the nearness of T_N to the superfluid transition of the He^4 bath, making the pumping rate difficult to control in this region. A value of $T_N = 2.185^\circ\text{K}$ compares with 2.24°K obtained by Forstat, Love, and McElearney⁹ from the specific heat.

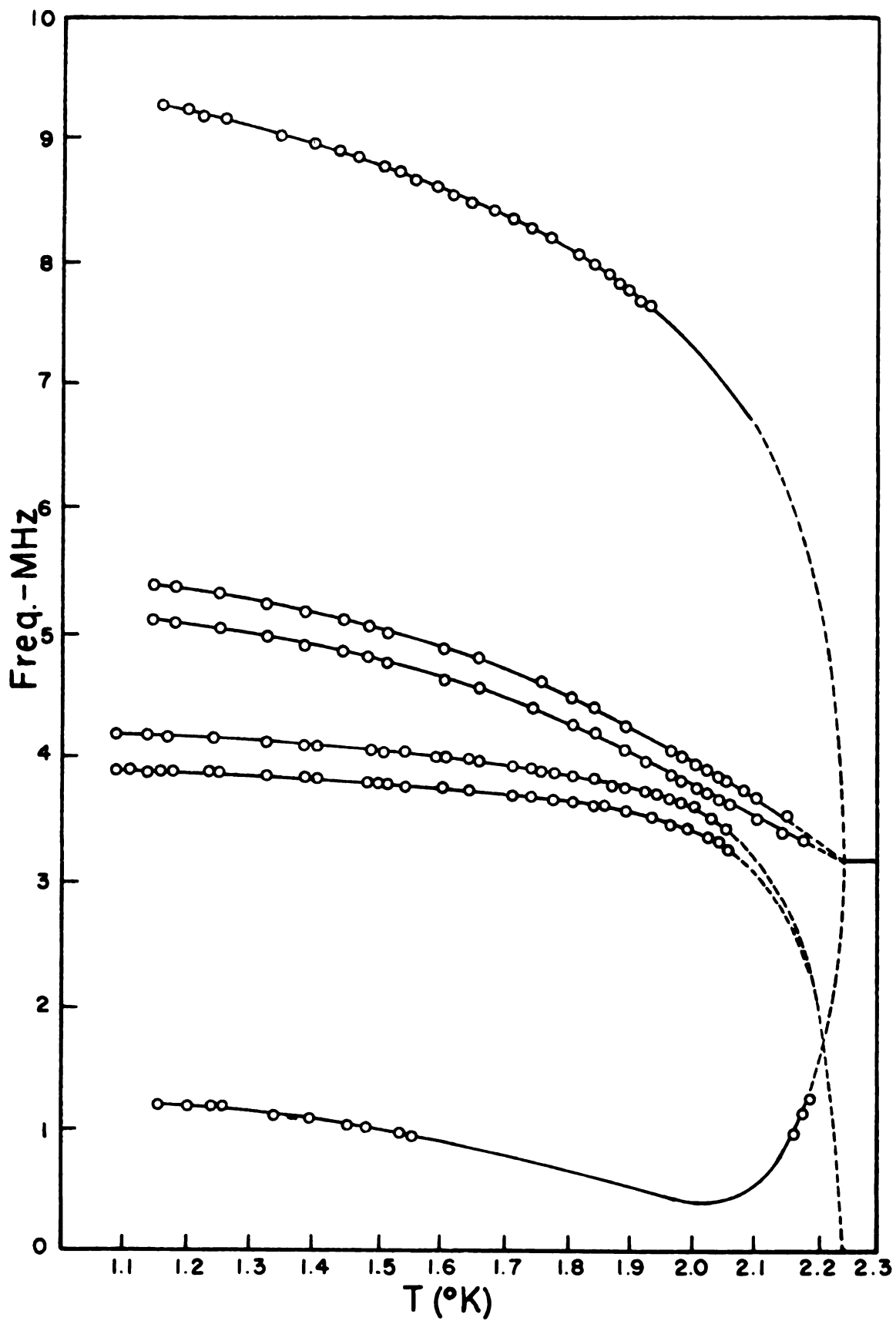


Figure 5.-- Temperature Dependence of the Rb^{87} Resonance Frequencies

The six lines in the spectrum represent all possible transitions among the four energy levels for $I = \frac{3}{2}$ and, if they are designated $\nu_1 > \nu_2 > \nu_3 > \nu_4 > \nu_5 > \nu_6$, they are interrelated.

$$\nu_1 = \nu_2 + \nu_5 = \nu_3 + \nu_4 \quad (38)$$

$$\nu_6 = \nu_2 - \nu_4 = \nu_3 - \nu_5 \quad (39)$$

The transitions and their relations are illustrated in Figure 6.

The magnitude of the internal field was calculated from equation (12) and this field is plotted as a function of temperature in Figure 7. The energy levels were calculated from the frequencies at various temperatures and combined with the internal field at those temperatures to yield Figure 8 which shows the variation of the energy levels in frequency units with the internal field. The direction of the internal field was calculated from equation (16) as described in Section II-B. The results are summarized in Table VI.

The resonance spectrum of Rb^{85} in the ordered state consists of four lines, and their temperature dependence is shown in Figure 9. The frequencies of these lines vary little with the temperature because the Hamiltonian is dominated by the temperature independent quadrupole interaction. The Rb^{85} lines were a good deal weaker than the Rb^{87} lines because, while Rb^{85} is nearly three times more

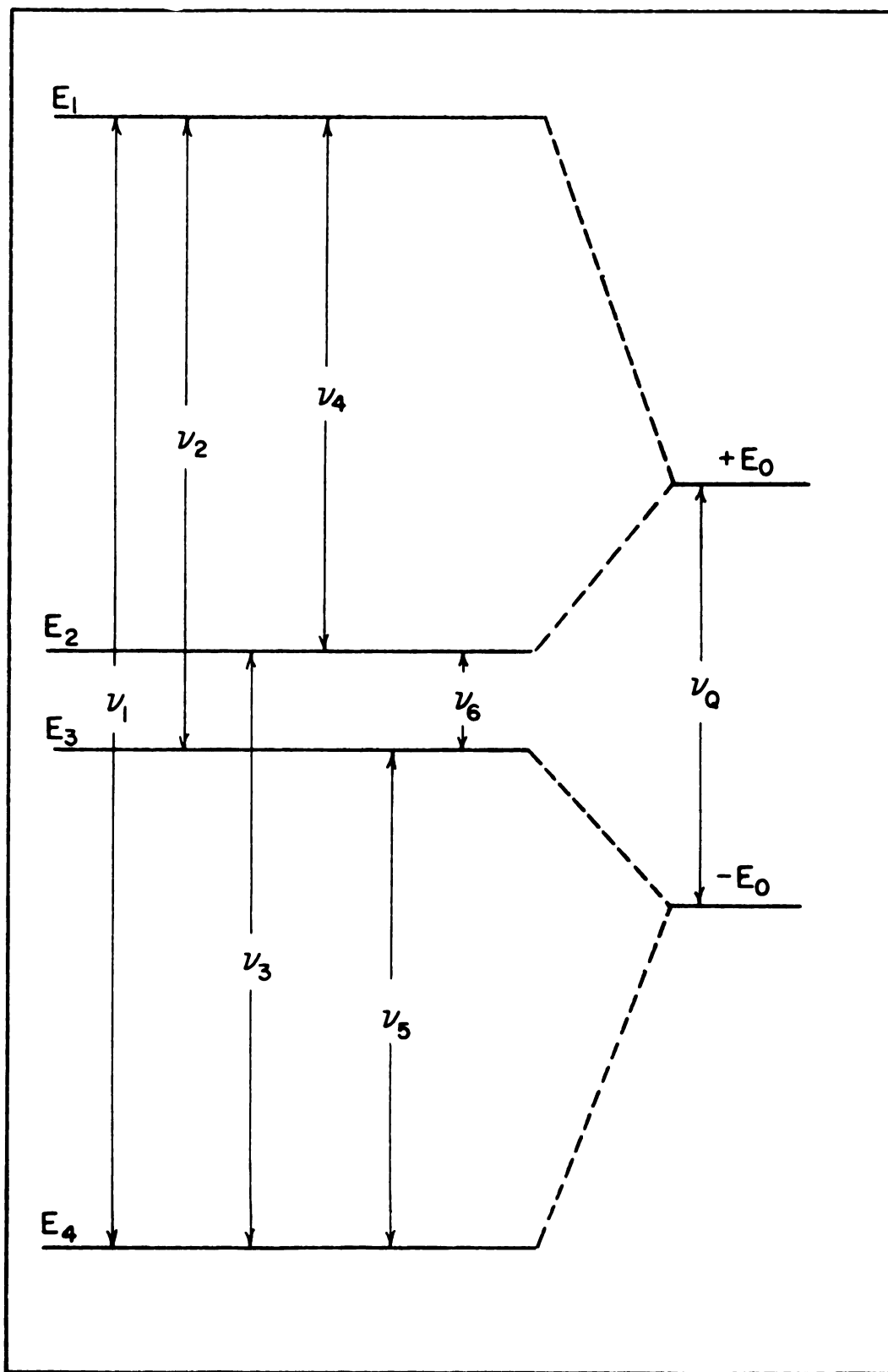


Figure 6.--Relations between Transitions and Energy levels
for Rb^{87}

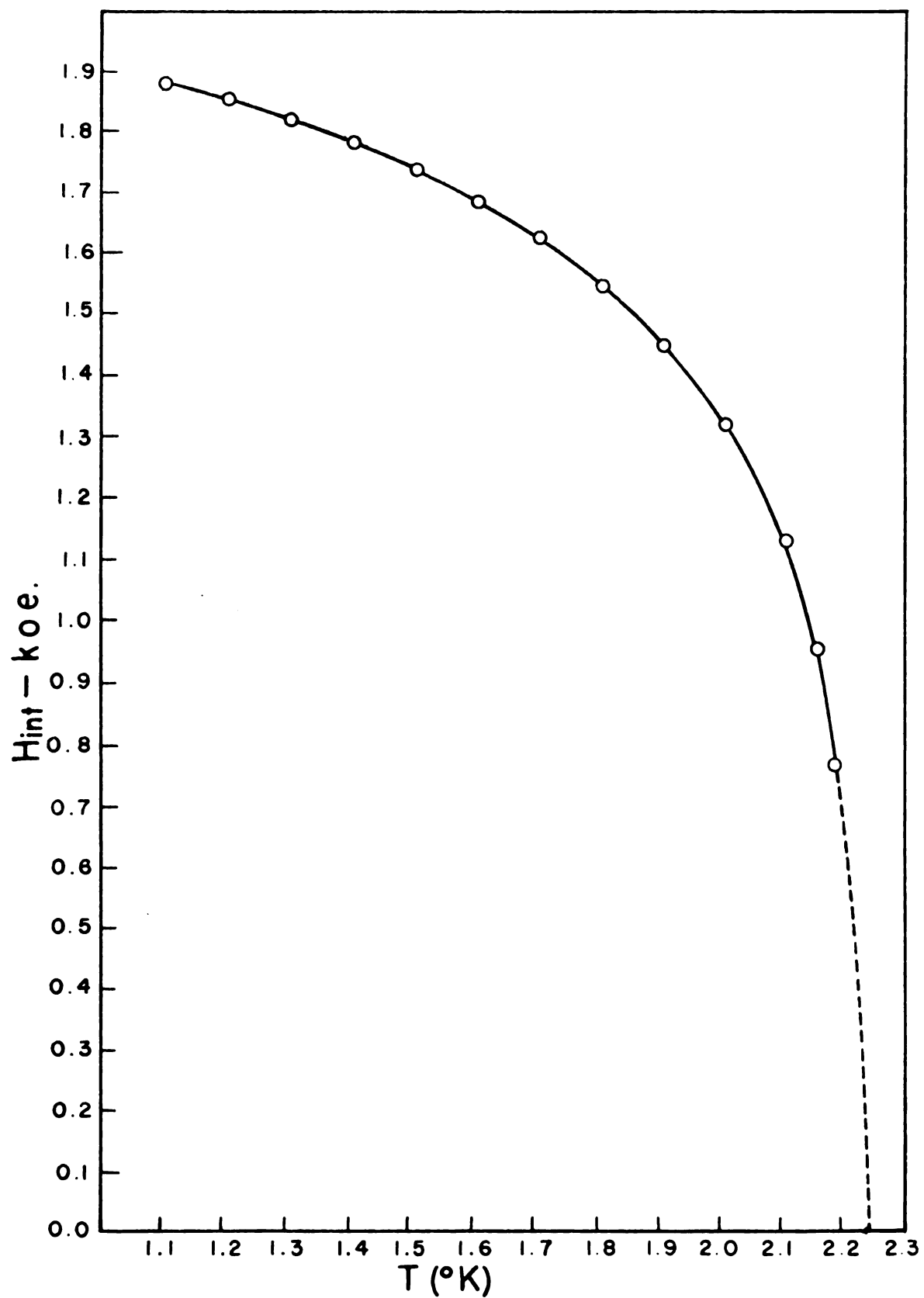


Figure 7.--Temperature Dependence of the Rubidium Internal Field

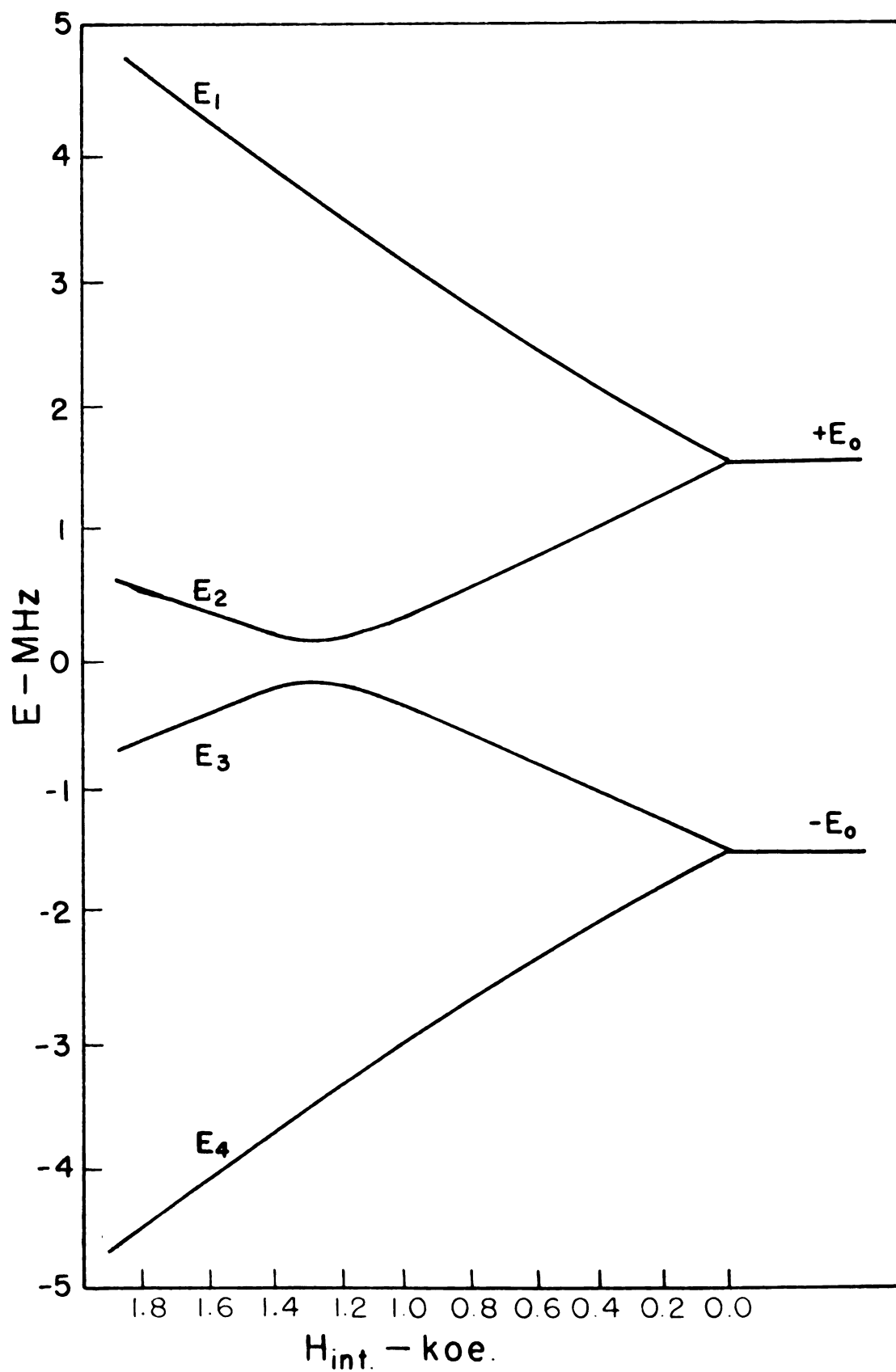


Figure 8.--Variation of the Rb^{87} Energy Levels with the Internal Field

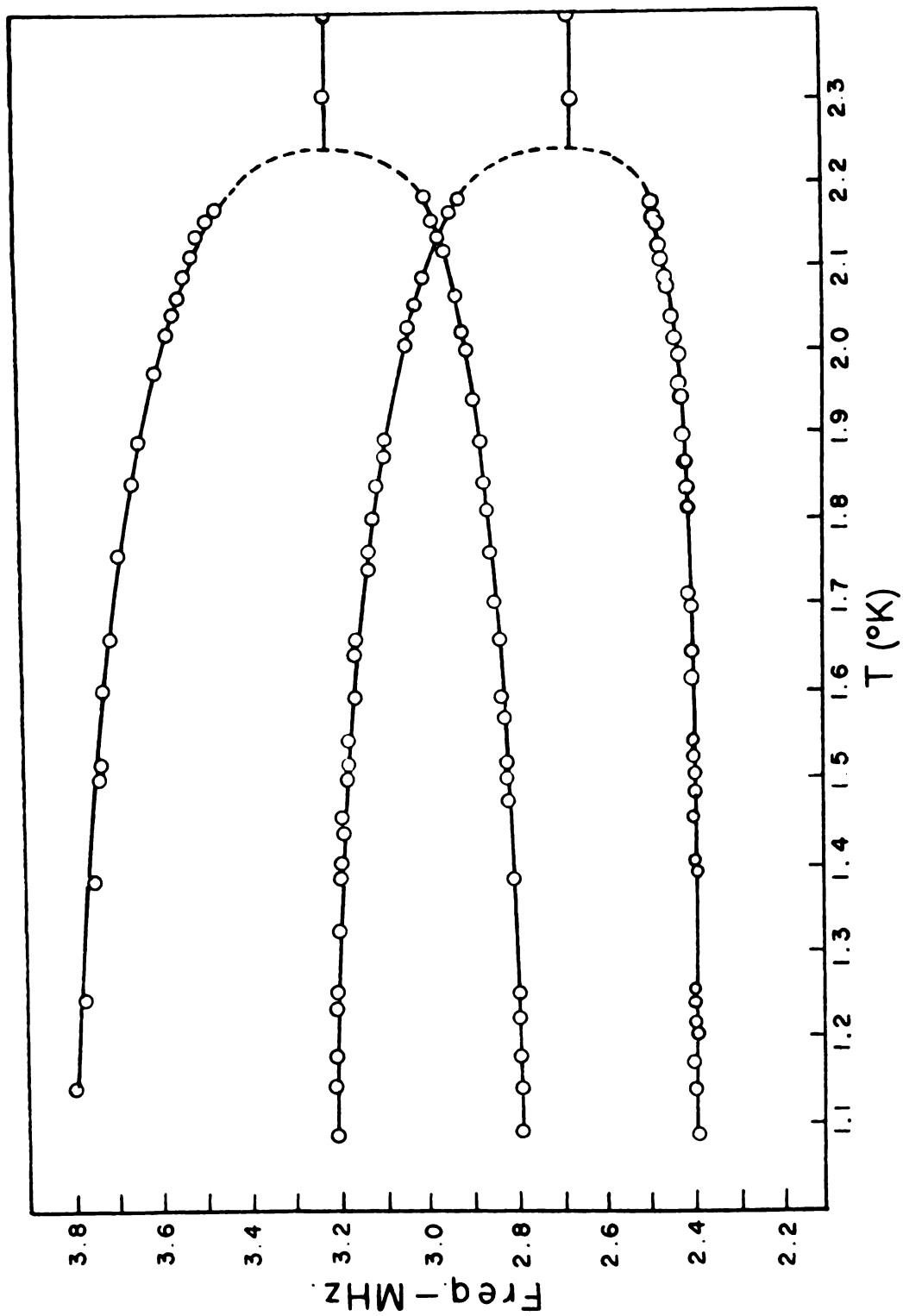


Figure 9.1.--Temperature Dependence of the Rb^{85} Resonance Frequencies

abundant, the ratio of the transition probabilities is proportional to the square of the ratio of the magnetic moment.

$$\frac{W_{85}^{85}}{W_{87}^{87}} \propto \left(\frac{\gamma_{85}}{\gamma_{87}} \right)^2 = 0.087 \quad (40)$$

D. Internal Fields

Table VI summarizes the magnitudes and directions of the local fields found at the proton, rubidium, and chlorine sites. The magnitudes given in the table were measured at 1.1°K and the directions are given in terms of the angles χ , ψ , and ω measured from the $\vec{a}$, $\vec{b}$, and $\vec{c}$ axes respectively. The directions of the measured fields are shown in the stereogram in Figure 14.

Table VI. Orientation and Magnitude of Internal Fields

Site	Magnitude at 1.1°K (koe)	χ with a	ψ with b	ω with c
proton I	4.439	60	30	55
proton II	4.296	35	65	54
rubidium	1.879	128	123	70
chlorine A	19.49	62	39	42
chlorine B	21.63	57	42	44

E. Magnetic Space Group

The magnetic space group has been fixed as $P_s \bar{1}$ by the proton applied field resonance patterns, but the direction of antitranslation represented by "s" remains to be determined. According to Opechowski¹⁰ there is only one nontrivial magnetic Bravais lattice in the triclinic system. It is generated by three primitive translations one of which is primed. Thus the magnetic lattice may be described by two normal translations and one antitranslation.

The set of primitive translations which characterize a triclinic lattice is not unique. If the set $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ generate a lattice, a number of other sets can be made from these vectors which will also generate the same lattice, such as $(\vec{a}_1 + \vec{a}_2)$, $\vec{a}_2$, $\vec{a}_3$, or $(\vec{a}_1 + \vec{a}_2 + \vec{a}_3)$, $\vec{a}_1$, $\vec{a}_3$. In general the new sets of primitive translations can include the edges, the face centers, and the body diagonal of the original primitive cell.

The set of primitive translations which describe the chemical lattice of $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ was chosen to make the lengths of the translations as short as possible. These primitive translations, namely $\vec{a}$, $\vec{b}$, and $\vec{c}$ are not necessarily identical to the translations which generate the magnetic lattice. The magnetic lattice is subject to two conditions. One of its primitive translations must be primed and secondly these translations must be the edges,

face diagonals, or body diagonal of the chemical unit cell. There exists a lattice in which the magnetic symmetry can be described with an antitranslation in only one direction, but the same symmetry described in the particular lattice formed by $\vec{a}$, $\vec{b}$, and $\vec{c}$ may require more than one direction of antitranslation.

By considering the primed direction of the magnetic lattice to be successively an edge, a face diagonal, and a body diagonal of the chemical cell, it can be shown that the magnetic symmetry when represented in the chemical unit cell may require one, two, or three directions of antitranslation.

Figure 10 shows the triclinic magnetic lattice P_S . The open and solid circles are used to distinguish primed from unprimed translations. Translations between two circles of different kinds are antitranslations while those between circles of the same kind are normal translations. Thus the magnetic lattice is generated by a primed translation $\vec{X}_1$, and two unprimed translations $\vec{X}_2$ and $\vec{X}_3$.

The chemical cell is shown in Figure 11 with the antitranslation chosen as an edge. The vectors represent the primitive translations of the magnetic lattice. The same arrangement of open and closed circles can be represented by the chemical cell with one direction of antitranslation.

The antitranslation has been chosen as a face diagonal of the chemical cell in Figure 12. This symmetry

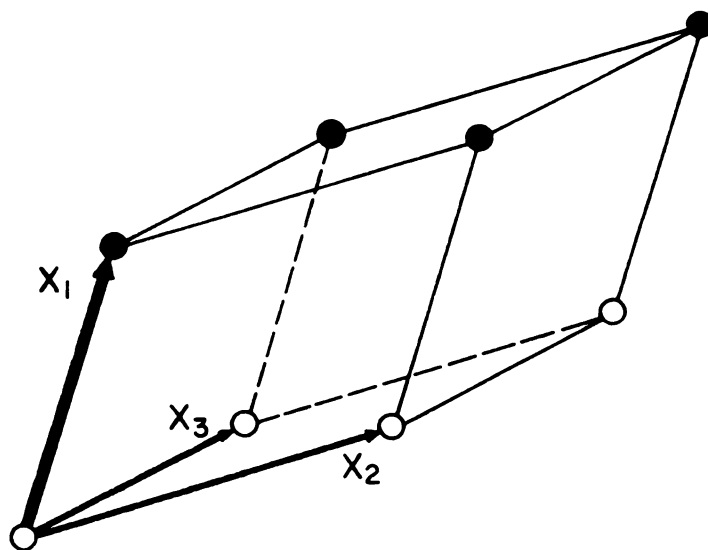


Figure 10.--Magnetic Bravais Lattice P_s

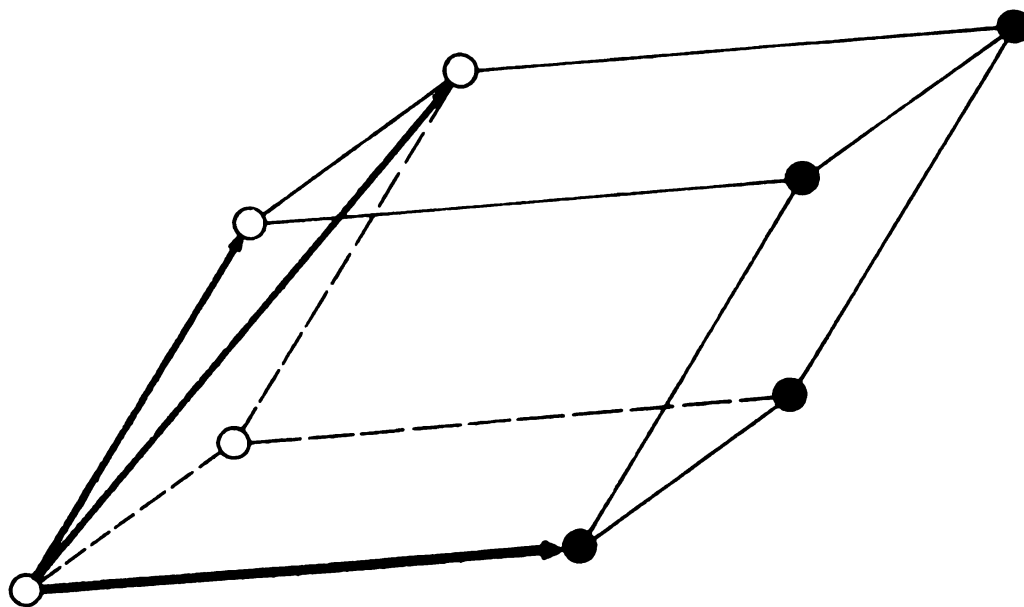


Figure 11.--Chemical Cell with an Antitranlation along One Edge

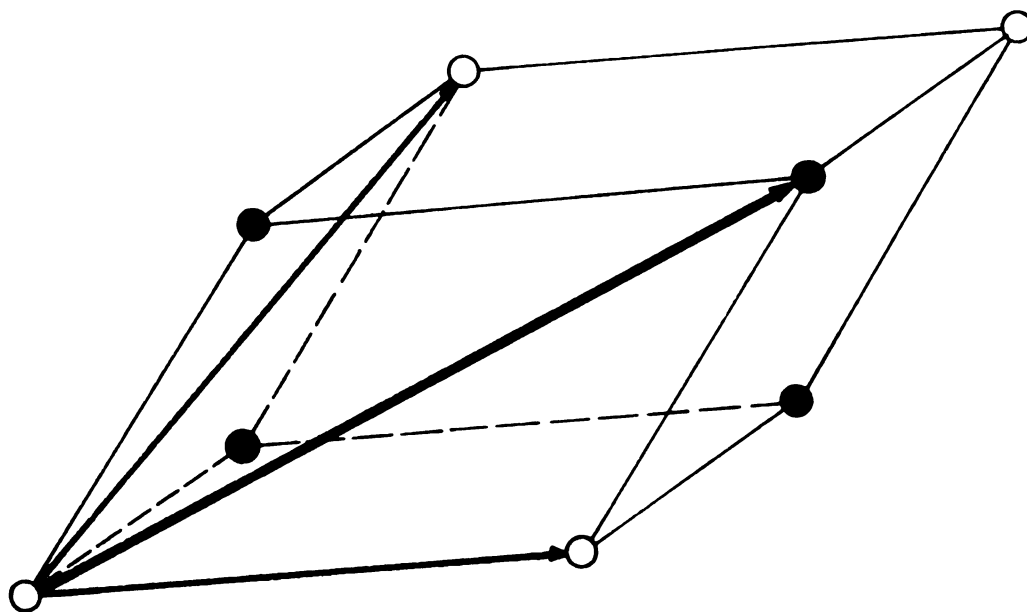


Figure 12. -- Chemical Cell with an Antitranslation along a Face Diagonal

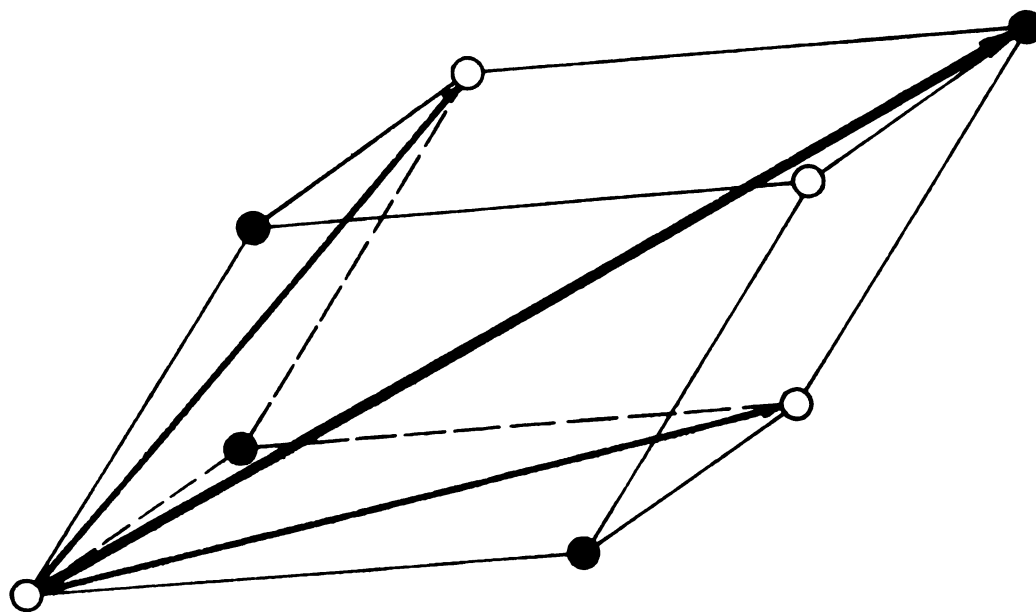


Figure 13. -- Chemical Cell with an Antitranslation along the Body Diagonal

can be described by one direction of antittranslation using the set of primitive translations shown, but in the chemical cell it requires two directions of antittranslation.

In Figure 13 the body diagonal of the chemical cell has been chosen as the antittranslation. It requires three primed translations to represent the same symmetry in the chemical lattice.

The preceding figures have shown that in the triclinic system the magnetic symmetry, while expressible in a proper magnetic lattice, may require one, two, or three antittranslations for its description in the chemical lattice. Thus the direction of antittranslation in the $P_5\bar{1}$ can be any of seven possibilities: $\vec{a}$, $\vec{b}$, $\vec{c}$, $\vec{a}$ and $\vec{b}$, $\vec{a}$ and $\vec{c}$, $\vec{b}$ and $\vec{c}$, and $\vec{a}$, $\vec{b}$ and $\vec{c}$.

The dipolar local fields at the proton and rubidium sites were calculated on an electronic computer for each of the possible antittranslations. The chemical cell dimensions, the positions of the manganese, hydrogen, and rubidium atoms, and the direction of magnetization were read into the computer which formed the sum shown in equation (20) for all magnetic ions within a sphere of fixed radius. The direction of magnetization was taken parallel to the chlorine internal fields and the radius of the sphere was $40 \text{ \AA}$ which included roughly one thousand magnetic ions. The magnetic moment at 1.1°K was calculated by extrapolating the temperature dependence of the proton frequencies to 0°K , and calculating

the fractional change between 0° and 1.1°K . Then

$$\mu(1.1^\circ) = \frac{v_p(1.1^\circ)}{v_p(0^\circ)} \mu(0^\circ) \quad (41)$$

where the saturation magnetic moment was taken as five Bohr magnetons.

The proton local field is largely determined by the orientation of the nearest magnetic spin and is not sensitive to the various antitranslations. Thus reasonable proton fields were obtained for each of the seven possibilities, indicating that the direction of magnetization was chosen properly, but not selecting the proper directions of antitranslation. The directions of the calculated rubidium local fields, however, were strongly dependent on the direction of antitranslation. Figure 14 shows in a stereographic projection the measured rubidium field and the fields calculated for each of the possible antitranslations. Only that field corresponding to antitranslations in both the $\vec{a}$ and $\vec{b}$ directions lies close to the measured field. Table VII shows the magnitudes and directions of the fields calculated for this set of antitranslations. The magnetic spin arrangement is shown in Figure 15.

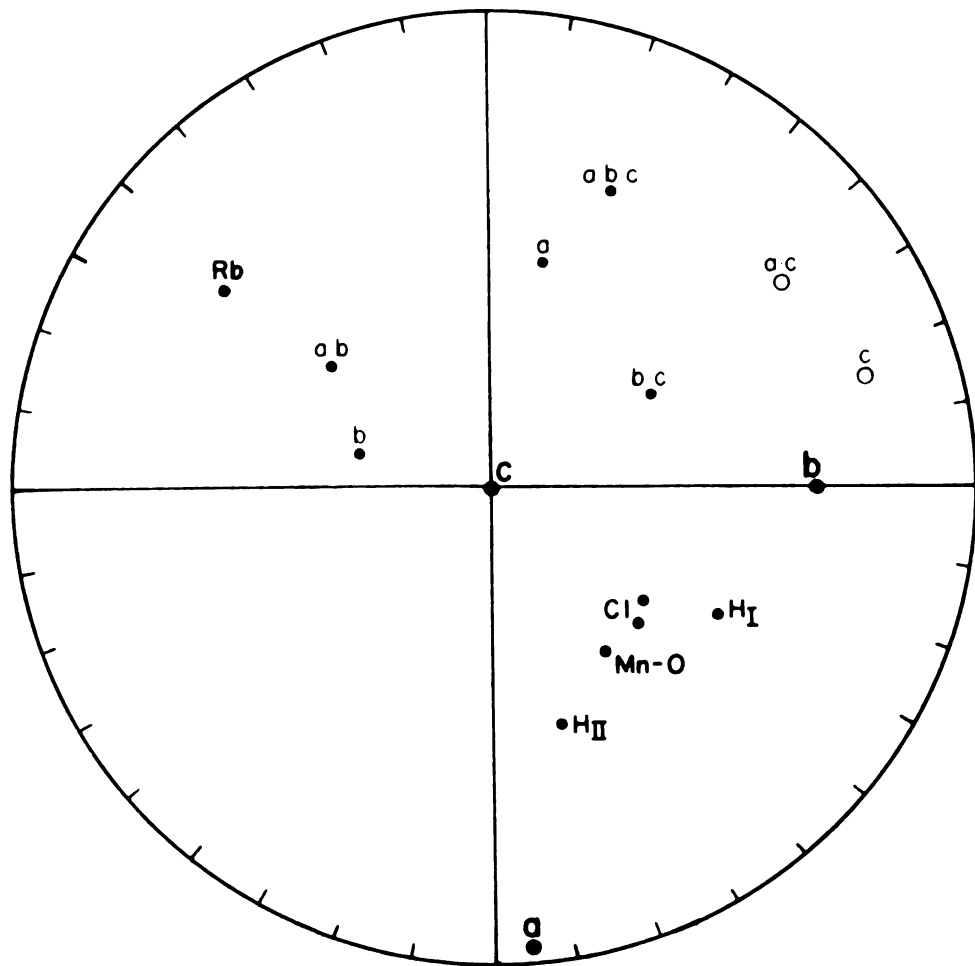


Figure 14.--Stereogram Showing the Observed Internal Fields
and the Calculated Rubidium Fields

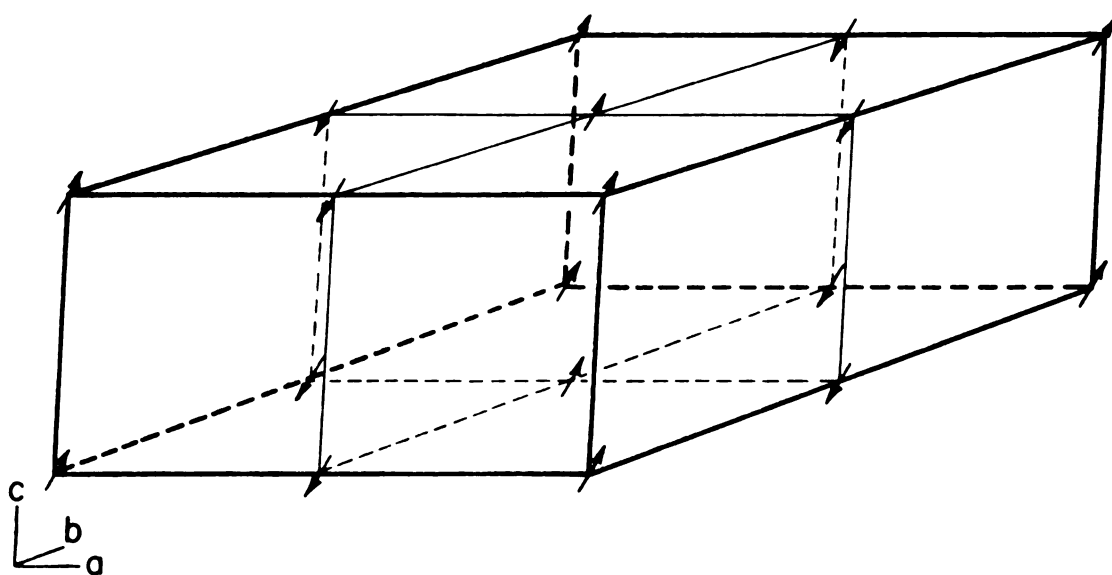


Figure 15.--Spin Arrangement for the Magnetic Space
Group $P_{a,b}^1$

Table VII. Calculated Internal Fields

Site	Magnitude Oersteds	χ with a	ψ with b	ω with c
proton I	4,177	54	38	51
proton II	4,223	35	75	53
rubidium	1,768	117	102	44

F. Discussion of Errors

The agreement between the calculated internal fields and the observed fields is indicated in Table VIII which lists the percentage differences in the magnitudes and the angular differences measured along a great circle. The agreement is quite good for the protons particularly since their positions are only based on a hydrogen bonding scheme. This indicates that the direction of the chlorine internal fields is a good approximation to the magnetization.

Table VIII. Difference between Observed and
Calculated Local Fields

Site	Magnitude %	Angle along a Great Circle
proton I	5.9	7.5
proton II	1.7	10.0
rubidium	5.9	24.5

The direction of the rubidium field is not in such good agreement. This is not simple to explain, because the direction of the internal field was determined more accurately than the protons and presumably the X-ray determination of the rubidium atomic coordinates is quite accurate. The method of moments can be applied to any three lines in the spectrum of a nucleus with spin $I = 3/2$. The direction of maximum splitting was found for five Rb^{87} lines and different sets of these lines were used in three calculations of the internal field direction. The field directions obtained from these calculations were all within ten degrees of each other. The rubidium internal field was calculated for a few directions of antitranslation with the magnetization direction taken along the manganese to oxygen bond. The magnitudes and directions differed slightly from those calculations with the magnetization along the chlorine fields but not enough to explain the discrepancy in terms of inaccuracy in the magnetization direction.

One possible explanation that remains is that the rubidium field is not due entirely to magnetic dipolar effects. The fact that the observed and calculated field directions and the magnetization direction are nearly coplanar, suggests that the observed internal field is the result of dipolar fields and a nonvanishing magnetization at the rubidium site. Even a small value of the magnetization could be sufficient to combine with the dipole field to yield a net field in the observed direction.

G. Anisotropy Energy

The exchange field H_e can be estimated from the transition temperature

$$\mu H_e = kT_N \quad (42)$$

where μ is the manganese magnetic moment and k is Boltzmann's constant. This yields a value for $H_e = 6.66$ koe.

The spin flop critical field, H_c , is related to the exchange field and the anisotropy field H_a .¹¹

$$H_c \approx \sqrt{2H_e H_a} \quad (43)$$

This relation is based on the molecular field approximation and is most nearly exact at absolute zero. Since a search for the spin flop transition at 1.1°K indicates that the critical field is not below 8.3 koe then the anisotropy field must be greater than 5.2 koe.

Computer calculation of the principle axes of the tensor in equation (22) indicates that the dipole-dipole effect does not make a significant contribution to the anisotropy energy. None of the axes lies very close to the direction of magnetization and the field produced at one manganese site by the other manganese ions in the lattice is only about 750 oersteds.

The axis of local symmetry at the manganese site is the manganese to oxygen bond. The effect of the crystalline field is to align the spins in this direction and it is

significant that this bond direction is close to the chlorine internal fields as shown in Figure 14. Thus the direction of magnetization is determined almost entirely by the crystalline field.

In conclusion, continued investigation in this area seems worthwhile. The search for the spin flop transition should be extended to higher fields, in order to map the phase diagram; and the effects of the relative magnitudes of the exchange and anisotropy fields may bear further study.

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