ORDERED MAGNETIC SYSTEMS STUDIED
BY NUCLEAR ORIENTATION

by

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in

The Department of Physics

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Abstract

The antiferromagnetic and spin-flop phases of MnCl$_2$·4H$_2$O have been investigated by observing the nuclear orientation of $^{54}$Mn in that material. The sublattice magnetizations in the absence of an external field were found to lie in a direction between the a and c crystal axes at an angle of 11.5° ± 3.5° to the c axis. The field dependence of the spin configuration in the spin-flop state indicates that second order anisotropy is significant in this system. The molecular fields were determined by combining the results of this work with other measurements of the critical fields (Rives and Benedict, 1975). The results are: the exchange field is 11.05 ± 0.21 KOe; the biaxial single ion anisotropy fields are 0.75 ± 0.22 KOe and 2.35 ± 0.23 KOe along the a* and b axes respectively; the second order anisotropy field is 1.45 ± 0.19 KOe and the anisotropic exchange field is 0.1 ± 0.3 KOe.

The spin-flop transition region was found to be adequately described by a 'domain' structure in which regions of antiferromagnetic phase and regions of spin-flop phase co-exist in the crystal.
Measurements were made of the temperature dependence of the spin-flop transition field and, contrary to the extrapolated results of Rives and Benedict (1975), the spin-flop field was found to decrease with decreasing temperature from 0.3K to 0.15K. If there is a minimum in the transition field it must occur at lower temperatures.

The cooling of the MnCl$_2$·4H$_2$O crystal which was held in contact with a copper heat sink by Apiezon N grease was fitted to the relation $Q = kA(T_1^n - T_2^n)$ where $T_1$ and $T_2$ are the temperatures of the crystal and copper heat sink respectively, and $A$ is the contact area. For $n = 4$ the value obtained for the constant $k$ is $(8.2 \pm 1.9) \times 10^3$ ergK$^{-4}$ sec$^{-1}$ cm$^{-2}$.

Nuclear orientation experiments were also performed on the systems $^{103}$Ru-Fe and $^{59}$Fe-Fe. The gamma-ray anisotropies for these systems (at temperatures of 10 and 15 mK, respectively) were very small; however, it was possible to determine limits for the magnitudes of the nuclear magnetic moments of the active nuclei. The $^{103}$Ru moment was found to be greater than 0.15μN and the $^{59}$Fe moment was found to be less than 0.9μN.

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CHAPTER I
Introduction

The observation of nuclear orientation of nuclei in a magnetic solid depends on the hyperfine interaction and the character of the decay scheme. Consequently the nuclear orientation technique can give solid state or nuclear physics information or both. The experiments described in this thesis involve both these fields. The dominant part of the work involves a study of the antiferromagnet $\text{MnCl}_2\cdot4\text{H}_2\text{O}$. This is discussed in the first three chapters. The remaining chapters describe experiments yielding predominantly nuclear physics information concerning the nuclei $^{59}\text{Fe}$ and $^{103}\text{Ru}$.

1.1 Nuclear Orientation

Following Blin-Stoyle and Grace (1957), the angular distribution of gamma radiation from oriented nuclei is given by

$$W(\theta) = \sum_{K \text{ even}} B_K U_K P_K (\cos \theta) , \quad (1.1.1)$$

where $\theta$ is the angle between the axis of detection of the radiation and the axis of quantization and $P_K$ is the
Legendre polynomial. $U_K$ and $F_K$ depend on the nuclear parameters and are discussed in detail in section 4.1. The parameters $B_K$ completely describe the state of orientation of the initial system. For a nuclei with spin $I$ the $B_K$ (for $K \leq 2I$) are given by

$$B_K = \sum_m (2K+1)^{1/2} C(2I; mO) w(m) ; K \leq 2I$$

where $C$ is the Clebsch-Gordon coefficient and $w(m)$ is the normalized population of the substate with magnetic quantum number $m$. If the nucleus, with magnetic moment $\mu$, experiences a hyperfine field $H_{hf}$, the ground state is split into $2I+1$ equally spaced Zeeman levels separated in energy by $\mu H_{hf}/I$. In thermal equilibrium the population of these levels is given by the Boltzmann distribution so that the normalized population of a level is

$$w(m) = w_0 \exp(-\mu H_{hf} m/IKT),$$

where $w_0$ is the normalization constant.

If the detection axis is given by a unit vector $D$ and the axis of quantization by a unit vector $M$ then the above expression for $w$ (equation 1.1.1) becomes

$$W(D) = \sum_k \lambda_k P_K(D \cdot M)$$

where $\lambda_k = B_k U_k F_k$. For an antiferromagnet the crystal
lattice is composed of separate magnetic sublattices. The
directions of the sublattice magnetizations $M_i$ define the
nuclear orientation axes through the hyperfine interaction.
If the sublattices have relative populations $p_i$ then

$$W(D) = \sum_{ik} p_i A_k P_k (D \cdot M_i).$$

If $U_K$, $F_K$ and the hyperfine interaction are known, a
measurement of the angular distribution of the gamma-rays
allows the determination of the temperature $T$ of the spin
system (through the $A_K$ terms), the sublattice magnetization
axes $M_i$ (through the $P_k$ terms) and the relative
populations $p_i$. For two equal sublattices $p_1 = p_2 = \frac{1}{2}$.

In this work the quantity $1 - W(D)$ is called the
'anisotropy'.

1.2 Theory for an Antiferromagnetic Insulator

1.2A Simple Molecular Field Theory

The general field dependent behavior of an
antiferromagnet can be explained by considering a simple
model (e.g. Martin, 1967). Assuming a Heisenberg
interaction between two spins $S_1$ and $S_2$, the interaction
energy is given by

$$F_{ext} = J S_1 \cdot S_2.$$
where $J$ is the exchange constant and is positive. The preference for the spins to lie along a fixed axis in the crystal, the easy axis, is given by an anisotropy term (uniaxial) (Nagamiya et al. 1957) of the form

$$F_{an} = -\frac{1}{2} J \cos^2 \phi$$

where $\phi$ is the angle between the easy axis and the spin axis. In addition application of a magnetic field produces an interaction (where $\mu_B$ is Bohr magneton and $g$ is the gyromagnetic g-factor)

$$F_H = -H \cdot S \quad (\mu_B g)$$

Using the notation of fig. 1.1 the total free energy $F$ for $N$ spins is given by

$$\frac{F}{N} = S^2 J \cos(\alpha - \beta) - \frac{1}{2} L (\cos^2 \alpha + \cos^2 \beta) - g \mu_B S H [\cos(\alpha + \psi) + \cos(\beta + \psi)].$$

On minimization of the energy it is seen that the spin system can exist in three distinct phases for the field applied along the easy axis. At low fields the spins are aligned antiparallel along the easy-axis ($\alpha=0$, $\beta=\pi$). For large fields the paramagnetic state occurs in which the spins are both parallel to the applied field ($\alpha=\beta=0$). For intermediate fields the spin-flop state occurs for which $\alpha=-\beta=\theta$. The transition from the antiferromagnetic phase to the spin-flop phase occurs in thermal equilibrium
Figure 1.1  Notation for the Spin Angles.
at a field

\[ \mu' H_{th} = [L(2J-L)]^{\frac{1}{2}} \]

where \( \mu' = g_\mu_B/S \).

The spin-flop angle \( \theta \) is given by

\[ \cos \theta = \mu' H/(2J-L) \]

The transition from the spin-flop to paramagnetic state takes place when \( \cos \theta = 1 \) which occurs in a field given by

\[ \mu' H_{pz} = 2J-L \]

If the applied field is perpendicular to the easy-axis there is a transition from the antiferromagnetic phase (\( \alpha=\pi-\beta=\theta \)) to the paramagnetic phase (\( \alpha=\beta=\frac{\pi}{2} \)) at a field

\[ \mu' H_p = 2J+L \]

The spin direction in the antiferromagnetic state is given by

\[ \sin \theta = \mu' H/[2J+L] \]

The spin-flop transition (\( H_{th} \)) is a first order of transition because a finite change in magnetization occurs. In fact there exists a possible hysteresis at the transition. The antiferromagnetic state is stable up to the field

\[ \mu' H^+ = [L(2J+L)]^{\frac{1}{2}} \]
whereas the spin-flop state is stable down to a minimum field given by

\[ \mu' H^- = (2J-L)[L/(2J+L)]^\frac{1}{2} \]

The transition to the paramagnetic state is continuous in the magnetization. It is therefore second order and no hysteresis is expected.

The interactions are commonly given in terms of effective fields. These are defined by the following expressions

\[ H_E = JS/g\mu_B ; \quad H_A = LS/g\mu_B \]

In this notation the energy is

\[ F/N = g\mu_B H_E \cos(\alpha-\beta) - \frac{g\mu_B H_A (\cos^2\alpha + \cos^2\beta)}{2S} - g\mu_B SH(\cos\alpha + \cos\beta) \]

The critical field \( H_{th} \) is given by

\[ H_{th} = [H_A (2H_E - H_A)]^\frac{1}{2} \]

1.2B General Mean Field Approach

The magnetic phase diagrams of antiferromagnetics have been studied in detail in terms of a more general molecular field approximation by several investigators including Nagamiya et al. (1955), Rohrer (1969), Blazey
et al. (1971), Yamashita (1972) and Morrison (1973).

Following Blazey et al. (1971) the free energy can be expressed by

\[ F/N = S^2 \left[ J \delta_A \delta_B \cos(\alpha - \beta) + \frac{1}{2} J' (\delta_A^2 + \delta_B^2) \right. \\
+ K_E \delta_A \delta_B \cos \alpha \cos \beta - \frac{1}{2} (K_{I1} - K') (\delta_A^2 \cos^2 \alpha + \delta_B^2 \cos^2 \beta) \right] \\
- g \mu_B S H [\delta_A \cos(\alpha - \psi) + \delta_B \cos(\beta - \psi)] \\
- T [s(\delta_A) + s(\delta_B)] ,
\]

where \( \alpha, \beta \) are the angles of the sublattice magnetization and \( \psi \) is the angle of the applied magnetic field \( H \) with the easy axis; \( \delta_A, \delta_B \) are the sublattice magnetizations relative to the \( T=0 \) value; \( J, K_E \) are the intersublattice exchange and anisotropic exchange interaction; \( J', K' \) are the intrasublattice exchange and anisotropic exchange interactions; and \( K_{I1} \) is single ion anisotropy. It is convenient to use the molecular fields defined by:

\[ H_E = JS/g \mu_B , \quad H_{K1} = (K_{I1} - K')S/g \mu_B \]
\[ H_{KE} = K_E S/g \mu_B , \quad H' = K'S/g \mu_B \]

The stability limits at \( T=0 \) between the antiferromagnetic and spin-flop phases are given by

\[ H^+ = \left[ (H_{K1} + H_{KE}) (2H_E + H_{K1} + H_{KE}) \right]^{\frac{1}{2}} \]
\[ H^- = (2H_E - H_{K1} + H_{KE}) \left[ (H_{K1} + H_{KE})/(2H_E + H_{K1} + H_{KE}) \right]^{\frac{1}{2}} ,\]
whereas the thermodynamic transition, for which the energies of the two states is equal is given by

$$H_{\text{th}} = (H^+ \cdot H^-)^{1/2}$$

$$= \left[ (H_{KL} + H_{KE})(2E_{KL} - H_{KL} + H_{KE}) \right]^{1/2}.$$  

For the paramagnetic transition

$$H_{\text{py}} = 2E + H_{KL} + H_{KE},$$

and

$$H_{\text{pz}} = 2E - H_{KL} + H_{KE},$$

for $H$ applied along the $y$-axis and $z$-axis (easy axis) respectively. In the spin-flop phase the spins make an angle $\theta$ with the applied field given by

$$\cos \theta = H / (2E + H_{KE} - H_{KL}).$$

It is found that there are critical points marking the end of the antiferromagnetic to spin-flop transition as the applied magnetic field deviates from the easy axis. These critical points are given by the critical fields

$$H_{\text{y}}^f = H_{KL} \left[ (H_{KL} + H_{KE}) / (2E - H_{KL} + H_{KE}) \right]^{1/2},$$

$$H_{\text{z}}^f = H_{\text{th}},$$

such that there exists a continuous transition (neither first nor second order) from the antiferromagnetic to spin-
flop phase. The critical condition is $\alpha + \beta = \pm \pi / 2$. The maximum angle of the applied field at which a first order transition can be observed at $T=0$ is

$$\tan \psi = \frac{H_x^f}{H_z^f}$$

For the case of orthorhombic symmetry, the uniaxial anisotropy term in the free energy, $\frac{1}{2}K_l (\cos^2 \alpha + \cos^2 \beta)$, must be replaced by a term (Nagayima et al., 1955)

$$\frac{1}{2}K_{lx} (\mu_A^2 + \mu_B^2) + \frac{1}{2}K_{ly} (v_A^2 + v_B^2)$$

where $\mu_{A,B}$ and $v_{A,B}$ are the direction cosines with the $x$ and $y$ axes respectively of the sublattice magnetizations. The $z$-axis will be the easy axis, and the $y$-axis will be the second easy axis if

$$0 < K_{ly} < K_{lx}$$

If we define

$$H_{Kly} = -\frac{K_{ly} S}{g\mu_B}$$
$$H_{Klx} = -\frac{K_{lx} S}{g\mu_B}$$

then all the above expressions retain the same form with $H_{Kl}$ replaced by $H_{Kly}$. In addition, the paramagnetic transition with the applied field in the $x$-direction is given by

$$H_{px} = 2H_E + H_{Klx} + H_{KE}$$
Consider the second single ion anisotropy which contributes a term in the above expression for the free energy of the form

\[-(N\mathbf{S}^2)^cK_2(\cos^4\alpha + \cos^4\beta)\]

In this case the field dependence of the spin orientation in the spin-flop state is given by (Morrison, 1973)

\[\cos\theta = \frac{H}{(H_0 - 2H_1K_2\cos^2\theta)}\]

where \(H_0 = 2H_E + H_{KE} - H_{K1}\) and \(H_1K_2 = K_2S/g\mu_B\).

The paramagnetic transition is then (putting \(\cos\theta = 1\))

\[H_{pz} = H_0 - 2H_1K_2\]

The paramagnetic transition for a field perpendicular to the easy axis is given by

\[H_{py} = H_0 + 2H_{K1}\]

If \(H_{K2}\cos\theta/H_E \ll 1\) the spin-flop transition point is given by

\[H^2_{th} = (H_{KE} + H_{K1} + H_{K2})H_0\]

1.2C Dynamics of the Spin-flop

The dynamics of the spin-flop transition have been considered recently by Keffer (1973) and Chow (1974). They have given a picture of the transition as follows:
in increasing field at a field $H_{\perp}^2 = H_E^2 + H_A^2$, which is less than the thermodynamic transition value $H_{th}$ the magnons of the surface layers of the crystal soften and surface-spin-flop regions develop. Similar regions might also develop near impurity clusters, dislocation lines and other imperfections. As the field $H$ approaches $H_{th}$ these regions develop in three dimensions and encompass the entire material. The system is continuously in stable equilibrium and the energy barrier is bypassed making the transition second order. Ideally, in a decreasing field the sequence is reversed. The transition takes place at the same field in increasing and decreasing fields; that is, there is no hysteresis.

1.2D. Spin Wave Theory

Quantum mechanical treatments of the spin-wave theory have been given by Anderson (1952), Zižman (1952) and Kubo (1952). In particular the low temperature behaviour of an anisotropic Heisenberg antiferromagnet in the neighbourhood of the magnetic phase boundaries has been studied by Feder and Pytte (1968) and Morozov (1972). Following Feder and Pytte we begin with the Hamiltonian

$$
= J \sum_{i,j} S_i \cdot S_j + K \sum_{i,j} S_{zi} S_{zj} \\
- L(\sum_i S_{zi}^2 + \sum_j S_{zj}^2) \\
- H(\sum_i S_{zi} + \sum_j S_{zj})
$$
where $J$, $K$ and $L$ represent respectively the exchange interaction, the anisotropic exchange and the single ion uniaxial anisotropy; and $\mu = g\mu_B$. The ordering is assumed to be of a simple two sublattice nature such that the $z$ nearest neighbours of an ion of one sublattice are on the other sublattice. For the antiferromagnetic phase the spin wave relation at $T=0$ (and neglecting zero point motion) becomes

$$\tilde{\omega}_w^0(k) = SzJ\left[(1+K' + 2L'\xi^2)^2 - \gamma^2(k)\right]^{1/2} \pm \mu H$$

where $K' = K/J$, $L' = L/zJ$, $\xi^2 = 1 - 1/2S$

$$\gamma(k) = z^{-1} \sum_{\rho} e^{-k \cdot \rho}$$

and $\rho$ gives the lattice position of a spin.

The transition from the antiferromagnetic to the spin-flop phase occurs at the field for which the frequency becomes zero. This occurs for $k = 0$ so that the transition occurs for $K' = 0$ at:

$$H^+ = 2SzJ[L'\xi^2(1+L'\xi^2)]^{1/2}$$

For the spin-flop state the spin wave dispersion relation becomes

$$\tilde{\omega}_w^0(k) = SzJ[1 + \gamma(k) + L'u^2 \cdot (1-\xi)]^{1/2} \times [1 + \gamma(k)(1-2\eta^2u^2) - Lu^2\xi(1+\xi)]^{1/2}$$
where \( u = \sin \theta \), \( \cos \theta = \mu H/[2SzJ(1+\frac{1}{2}K'-L\xi^2)] \)

and \( \eta_2 = 1 + \frac{1}{2}K' \). The spin-flop to antiferromagnetic phase boundary is determined by again setting \( w(k) = 0 \). This occurs for \( k = 0 \) and gives (for \( L \) type anisotropy only)

\[
\mu H^- = 2SzJ(l-L'\xi^2) x (L'\xi(1+\xi)/[2+L'\xi(1+\xi)])^{\frac{1}{2}}
\]

There is no need to introduce two sublattices in the paramagnetic phase so that the analysis is formally similar to the ferromagnetic system. The spin wave relation is

\[
hw^0(k) = \mu H - SzJ[l-2L'\xi^2 + k - \gamma(k)].
\]

The resulting transition point between the paramagnetic state and the spin-flop state is

\[
\mu H_{pz} = 2SzJ(1 + \frac{1}{2}K' - L'\xi^2)
\]

It is evident that the critical fields determined by spin wave calculations are the same as those calculated from the molecular field model provided one simply replaces \( L \) for the molecular field approximation by \( L\xi^2 \) for the spin wave case. It is also interesting to compare the magnetizations in the two models. The net magnetization \( <M_z> \) and the sublattice magnetization \( <M_z'> \) in the spin-flop state are related by

\[
<M_z> = 2<M_z'>\cos \theta
\]
In the molecular field case the sublattice magnetization \(<M_z'>\) is equal to \(M_0 = \mu_N g SN\) and is assumed constant for \(T=0\) in all fields. However, in the spin wave case the sublattice magnetization is an increasing function of \(H\) and equals \(M_0\) only in the paramagnetic phase. As the field is increased at constant temperature through the spin-flop range the net magnetization \(<M_z>\) increases through two contributions. Firstly, \(\cos \theta\) increases linearly with \(H\), and secondly the sublattice magnetization increases (becoming equal to \(M_0\) only at \(H_{pz}\)). Consequently \(<M_z>\) increases faster than linearly with \(H\), as contrasted with the strictly linear variation predicted by molecular field theory.

The thermodynamic transition between the antiferromagnetic and spin-flop states which can be determined by setting the free energies of the two states equal has not been determined. It would be of interest to know this transition point in the spin wave theory because many experiments on antiferromagnets show no hysteresis at the spin-flop transition.

1.3 Properties of MnCl\(_2\)·4H\(_2\)O

1.3A Crystallography

Several studies of the magnetic structure of MnCl\(_2\)·4H\(_2\)O have been made. The ionic positions and configu-
rations have been determined by x-ray analysis (Zalkin et al., 1964) and neutron diffraction (El Saffar and Brown, 1971). In addition the antiferromagnetic configuration has been determined without applied field by Altman et al. (1975) using neutron diffraction. It is a monoclinic antiferromagnet ($\beta = 99.7^\circ$) with four magnetic ions per unit cell. The crystallographic space group is P2$_1$/a ($C^5_{2h}$). A two sublattice collinear model fits the data for the antiferromagnetic state. The positions and spin assignments of the Mn$^{++}$ ions are given in Table 1.1. It was formerly thought that the easy axis was along the c-axis, but Altman et al. have determined that it is inclined between the c-axis and the c*-axis. The projection of the sublattice magnetizations on the a-c plane was found to be $6.9^\circ \pm 1.4^\circ$ from the c-axis towards the c*-axis (perpendicular to the ab plane). The projection on the b-c plane was $0.5^\circ \pm 0.5^\circ$ from the c-axis towards the b-axis.

1.3B Phase Boundaries

Measurement of the differential susceptibility is a particularly sensitive method to determine magnetic phase boundaries. This technique has been used by Rives (1967), and Rives and Benedict (1975) to determine the MnCl$_2$·4H$_2$O phase boundaries in temperatures down to 0.3K.
TABLE 1.1

Coordinates of the Manganese Spins

<table>
<thead>
<tr>
<th>Unit Cell Coordinates</th>
<th>Cartesian Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>x, y, z</td>
<td>1.571 1.627 6.178</td>
</tr>
<tr>
<td>x, y, z</td>
<td>0.565 7.886 0.085</td>
</tr>
<tr>
<td>(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)</td>
<td>7.688 3.130 2.969</td>
</tr>
<tr>
<td>(-\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z)</td>
<td>2.448 6.383 3.134</td>
</tr>
</tbody>
</table>

unit cell parameters

\(a_o = 11.186(6)\AA\)  \(b_o = 9.513(5)\AA\)
\(c_o = 6.186(2)\AA\)  \(\beta = 99.74(4)^\circ\)

---

\(^a\) Altman et al. (1975)
\(^b\) Zalkin et al. (1964)
They found that the spin-flop transition temperature dependence for temperatures less than 0.65K can be fitted by an equation of the form

\[ H_{pz}(T) = H_{pz}(0) (1 - AT^{3/2} + BT^{5/2}) \]

where

\[ H_{pz}(0) = 7.065 \text{ KOe} \]
\[ A = 0.066 \pm 0.007 \text{ K}^{-3/2} \]
\[ B = 0.129 \pm 0.020 \text{ K}^{-5/2} \]

This function has a minimum at 0.3K which was the lowest temperature point measured. They also studied the paramagnetic transition fields. Extrapolating these fields to zero temperature gives a measure of the molecular fields using a biaxial model. In particular, the zero temperature fields they obtain are

\[ H_{pz} = 18.55 \text{ KOe} \]
\[ H_{py} = 22.95 \text{ KOe} \]
\[ H_{px} = 24.55 \text{ KOe} \]

Using the equations of Sections 1.2B and 1.2D yields the following molecular fields

\[ H_E = 10.375 \pm 0.03 \text{ KOe} \]
\[ H_{Kly} = 2.20 \pm 0.05 \text{ KOe} \]
\[ H_{Klx} = 3.80 \pm 0.05 \text{ KOe} \]
In addition they fitted their data using the spin-flop transition point defined as

$$H^+ = \left( 2H_E H_A + H_A^2 \right)^{\frac{1}{2}}$$

to obtain the anisotropic exchange

$$H_{KE} = .00 \pm .025 \text{ KOe}$$

with the other fields unchanged. The experiments were performed on specimens which had been aligned to within ±2 degrees of the easy axis as determined by the minimum value of the transition point.

Other methods have been used to observe the phase boundaries. Gijsman et al. (1959) determined $H_{th}$ down to 1.0K using zero frequency electron resonance (with a signal frequency of 5 MHz) and nuclear magnetic resonance of the protons. M. Abkowitz and A. Honig (1964) performed paramagnetic and antiferromagnetic resonance at a frequency of about 24 GHz at temperatures as low as 0.32K. They obtained the 'critical field' resonance at 7500 Oe with a signal of 23.5 GHz at $T \approx 0K$. In addition a resonance at 6.0 KG was observed and one tending to 10.0 KG at $T=0$ was seen. These resonances occurred with the applied field along the c-axis. The linewidth of the critical field resonance was about 0.8 KG. Some hysteresis depending on
the direction of field sweep was observed in this resonance
(as high as 0.50 KG although samples with less than 0.10 KG
hysteresis were chosen to determine the critical field
values). The other two lines had a width of about 1.60 KG
and the low field resonance was observed only at low
temperatures (T < 0.6K). Another technique to study the
phase boundaries was used in an earlier study by McElearney
et al. (1967). They observed the magneto-caloric effect
at the spin-flop transition and obtained transition fields
with which the more accurate results of Rives and Benedict
are in agreement.

1.3C Specific Heat

Specific heat measurements of MnCl₂·4H₂O have
been reported by Miedema et al. (1965). In conjunction
with other experimental data they were able to determine
the coordination number q and the size of the exchange
interaction. The coordination number obtained is q = 6 and
the exchange interaction is J/k_B = 0.057K which give the
molecular field parameter

\[ H_E = 12.8 \text{ KOe} \]

This value of q = 6 corresponds to an approximately simple
cubic arrangement of the 3 pairs of nearest neighbours of
the manganese spins and is consistent with experimental
measurements of the Curie-Weiss constant $\theta$, the specific heat for $T \gg T_N$, the energy gained on transition to the antiferromagnetic state from the paramagnetic state at $T=0$, and the zero field susceptibility.

Also the nuclear specific heat was determined. Assuming an interaction of the form

$$\mathcal{H} = AS \cdot I$$

the nuclear heat capacity for $T \gg A/k_B$ is given by

$$C_N T^2 / R = I(I+1) S^2 A^2 / 3k_B^2$$

The value of $C_N T^2 = 2.6 \times 10^{-2}$ JK/mole determined by the experiments gives

$$A/k_B = 0.0131 \pm 0.00025 \text{ K}.$$
directions of the c and b axes. They found that the salts cooled very slowly; for example, it required six hours to achieve the measured maximum anisotropy. They suggested that this long cooling time was due to a long nuclear spin-lattice relaxation time, $T_1$. Miedema et al. (1965) observed, in the experiments described in sub-section 1.3c above that the time required to achieve thermal equilibrium at 0.1K was in excess of one hour. They suggested that fast cooling occurred for a small portion of nuclear spins, perhaps those with a short $T_1$ due to their proximity to magnetic impurities, followed by much slower cooling of the remaining spins.

The decay scheme (Lederer et al., 1964) for $^{54}$Mn is shown in figure 1.2. $U_K$ and $F_K$ coefficients for the angular distribution $W$ (equation 1.1.1) are

$$U_2 = 0.828, \quad U_4 = 0.418;$$

and

$$F_2 = -0.598, \quad F_4 = -1.079.$$}

The magnetic moment has been determined by Templeton and Shirley (1967) to be $\mu = 3.302 \mu N$. The hyperfine field of manganese in MnCl$_2$·4H$_2$O was determined from the nuclear specific heat (see section 1.3E following) to be $H = 645 \pm 12$ KG. The anisotropy as a function of temperature is given in figure 1.3 for axial and equatorial detection.
Figure 1.2 Decay Scheme of $^{54}_{\text{Mn}}$. 
Figure 1.3  Gamma-ray anisotropy for $^{54}\text{Mn}$ in MnCl$_2$·4H$_2$O.
1.3E NMR-ON

The observation of nuclear magnetic resonance in metals by the destruction of nuclear orientation (NMR-ON) has become a standard experimental technique. In the paramagnetic insulator La$_2$Mg$_3$(NO$_3$)$_2$·24H$_2$O the NMR of oriented $^{54}$Mn was observed by Neisen et al. (1968, 1970). The observation of NMR-ON in an antiferromagnet would provide information on the nuclear spin-lattice and spin-spin interactions, the electric quadrupole interaction, and would allow an accurate estimate of the hyperfine interaction.

Excitation of the nuclear magnetic resonance of oriented nuclei causes transitions between the magnetic levels with absorption of power thereby reducing the nuclear orientation. The effect of relaxation mechanisms on resonant absorption has been considered in a phenomenological approach by Bloch (1946). Consider a system of nuclei magnetized in the z-direction by a constant field $H_0$. Let $T_1$ and $T_2$ be the spin-lattice and transverse relaxation times respectively. If a radio-frequency field $H_1$, oscillating at the Larmor frequency $\omega_0 = \gamma H_0$ is applied in the x-y plane, the magnetization $M_z$ along the z-axis is given by

$$\frac{M_z}{M_0} = \frac{1}{1 + \gamma^2 H_1^2 T_1 T_2}$$
where $M_0$ is the magnetization in the absence of $H_1$ and $\gamma = \mu/Ih$. In this case the condition for saturation of the resonance is

$$S_0 \approx (\gamma H_1)^2 T_1 T_2 \approx 1.$$

Consider the value of $S_0$ for MnCl$_2 \cdot 4$H$_2$O at low temperatures. In an antiferromagnet the enhancement of the applied r.f. signal by the electronic susceptibility is not large. In fact, if the r.f. signal $H_{\text{lap}}$ is applied in the $x$-direction and $z$ is the direction of the sublattice magnetization then the magnetization rotates by an angle $\theta$ given by

$$\sin \theta = \frac{H_{\text{lap}}}{(2H_\text{E} + H_A)}$$

Since the hyperfine field follows the electronic magnetization an $x$-component is induced in the hyperfine field

$$H_{\text{lin}} = H_{\text{hf}} \sin \theta$$

The enhancement factor, $\eta$, for the r.f. signal is then given by

$$\eta = \frac{H_{\text{lin}}}{H_{\text{lap}}} \approx \frac{H_{\text{hf}}}{2H_\text{E}}.$$

For $H_{\text{hf}} = 600$ KG and $H_\text{E} = 10$ KG the enhancement is $\eta = 30$. 
Contributions to the transverse relaxation
time $T_2$ in an antiferromagnet come from the Suhl-Nakamura
spin-spin interaction (Suhl, 1959; Nakamura, 1958) and
Raman processes (for example see Jaccarino, 1965). For
normal isotropic concentrations the Suhl-Nakamura
interaction is dominant. This interaction which is
effective only between nuclei with identical gyromagnetic
ratios varies with the separation $R$ of the nuclei as

$$\frac{a}{R} \exp \left[ -\left( \frac{H_A}{H_E} \right)^{\frac{1}{2}} \frac{R}{a} \right]$$

where $a$ is the lattice spacing.

For our $^{54}$Mn in MnCl$_2 \cdot$4H$_2$O specimens in which
the concentration of the radioisotope is only $\sim 10^{16}$ mole$^{-1}$,
the neighbouring $^{54}$Mn spins are essentially out of the
range of this interaction. In this case, the Raman
processes which are independent of concentration dominate
the transverse relaxation rate which is given by

$$\frac{1}{T_2} = C \frac{T_\text{AE}^3}{T^4} \int_{T_\text{AE}}^\infty \frac{x dx}{e^{x^{-1}}}$$

where $T_\text{AE} = (2H_\text{E}H_A)^{\frac{1}{2}} g_B / k$ and where $C$ is a constant
depending on hyperfine and atomic parameters of the system.
$C$ has been calculated for MnF$_2$ to be $3 \times 10^7$ K-sec$^{-1}$
(Mitchell, 1957) and it has approximately the same value
for MnCl$_2 \cdot$4H$_2$O. We estimate that the value of $T_2$ is $\sim 1$ sec
at a temperature of 0.1K.
The spin lattice relaxation time for this system is also not readily determined theoretically. However, the specific heat measurements of Miedema et al. (1965) suggested a rather long relaxation time (>10 min) for the nuclear system whereas the results to be presented later indicate times of less than one hour. Hence, it is reasonable to estimate $T_1$ to be of the order of $10^3$ sec. Applying the values $n \approx 30$, $T_2 = 1$ sec, $T_1 = 10^3$s and $H_1 \approx 1$ mG, a value of $S_0 \sim 10^7$ is obtained so that the resonance should be readily observed.

The resonant frequency can be determined by the value of the hyperfine interaction measured from the specific heat (Miedema et al., 1965) of the $^{54}$Mn nuclear system. The hyperfine interaction is given by

$$\mathcal{H} = AS_z I_z$$

ignoring quadrupolar effects. The nuclear levels are split by

$$\hbar \nu_0 = AS_z$$

The hyperfine field is defined by

$$AS_z I_z = g_N \mu_N I_z H_{hf}$$
The $^{54}$Mn resonance is given by

$$\hbar \nu = \frac{^{54}g_N}{^{55}g_N}H_{hf}S_z = \frac{^{55}A}{^{55}g_N} S_z$$

The value of $^{55}A/k_B$ is $0.0131 \pm 0.0025$ K

and $^{54}g_N/^{55}g_N = -0.833$

Hence the results for $^{54}$Mn are $^{54}A/k_B = 0.0104 \pm 0.0002$ K

$$H_{hf} = 645 \pm 12 \text{ KG}$$

and $\nu = 542 \pm 10 \text{ MHz}$

1.4 Interactions in Antiferromagnetic Insulators

1.4A The Superexchange Interaction

Simple direct exchange interactions between atomic orbitals are not sufficient to account for the ordered magnetism found in many ionic solids. The long range interaction giving rise to the magnetic ordering is called superexchange.

It is clear that ligand wave functions are modified by the presence of a magnetic ion. Anderson (1950) considered the simplest such modification in which an electron is transferred from a ligand orbital (perhaps a filled 2p orbital) to an empty d orbital of the magnetic
ion. The inter-ionic exchange interactions then couple the magnetic and ligand ions in this excited state so that the ionic spins are aligned ferromagnetically or antiferromagnetically. If there is some distortion of the perfectly ionic configuration, due to overlap of the wavefunctions, the wavefunctions of the system are given in perturbation theory by small admixtures of excited states. Hence, the previously mentioned magnetic states will be admixed in the ground state of the system. Conservation of angular momentum will then require the ground state to have the same magnetic state (defined by the total angular momentum) as the lowest energy excited states. For example, an excited state with total spin equal to zero will only couple with a ground state of spin equal to zero. By this process a small admixture of excited states can lead to magnetic ground states with large exchange energy.

The admixture of an excited state can also be considered as a virtual transition. Such a transition is short-lived, does not conserve energy and cannot be detected by absorption or emission of radiation. The system is induced by the perturbation (of the ionic wavefunctions) to make a transition from the ground state to the excited states. The preferred spin of the excited state will then persist in the ground state. Only when
averaged over time does this model give the charge distribution of the true perturbed motion.

A more general approach to superexchange has been presented by Anderson (1969). One first considers a wave function of a magnetic ion surrounded by diamagnetic groups and in fact the whole lattice, excluding from the wavefunction the exchange effect of other magnetic ions. It is assumed that the exchange effects do not substantially disturb the ligand field wave function. The magnetic ions are then brought together and the exchange interaction is determined. This interaction is now the consequence of direct overlap of longer ranging orbitals. Since these orbitals are orthogonal, ferromagnetic interactions would be expected to result. However, excited states can be expected in which the magnetic electrons are on the same ligand field wavefunction. For the state with parallel spin momenta this interaction cannot occur, but for anti-parallel spins it gives a reduction in the total energy. This 'configuration mixing' favours antiferromagnetic interactions and is called 'kinetic exchange' by Anderson. The direct exchange favouring ferromagnetic alignment is called potential exchange.

For the case of MnCl$_2$·4H$_2$O the manganese ions are separated by non-linear chains of oxygen, chloride, and hydrogen ions. The details of the ligand fields and the
virtual transitions are extremely complicated in such a case. Nevertheless the form of the Hamiltonian can be given very simply, as follows.

For a pair of interacting ions each with a single unpaired electron the energy of the spin states relative to the mean value can be given by an effective exchange Hamiltonian (see for example Martin, 1967)

\[ \mathcal{H}_{\text{ex}} = -J_{ij}(\hat{s}_i \cdot \hat{s}_j) \]

For a Hamiltonian which contains no spin dependent terms the eigenstates of a pair of ions can be selected as eigenstates of \( S^2 \) and \( S_z \) where \( S = S_i + S_j \) and \( S_i \) is an ionic total spin. An effective Hamiltonian which generates such eigenstates is

\[ \mathcal{H}_{\text{ex}} = -J_{ij}(\hat{s}_i \cdot \hat{s}_j) + J'_{ij}(\hat{s}_i \cdot \hat{s}_j)^2 + \ldots \]

If the true Hamiltonian (not the effective Hamiltonian) of the system contains spin dependent terms such as spin-orbit coupling these can be treated separately as anisotropic interactions (see section 1.4B following). The first term in \( \mathcal{H}_{\text{ex}} \) should dominate. Then the total effect for an ionic solid can be represented by the exchange term

\[ \mathcal{H}_{\text{ex}} = -\sum_{ij} J_{ij} S_i \cdot S_j \quad (1.4.1) \]

This is the Heisenberg Hamiltonian.
The coupling between an electron of spin $S_i$ and the orbital motion of the same electron is given by

$$\mathcal{H} = \frac{\hbar}{2m^2c^2} \sum_i S_i \cdot (\text{grad} \cdot V(r_i) \times p_i)$$

where $p_i$ is the momentum of the electron and $V(r_i)$ is the potential. If the potential derives from a central force field the energy can be written in the form

$$\mathcal{H} = \sum_i \xi(r_i) l_i \cdot s_i$$

where $l_i$ is the orbital angular momentum and $\xi(r_i)$ is a function of the distance of the electron from the nucleus. There is a similar expression for the coupling of the spin of one electron and the angular momentum of another electron. For the case of states of given $L$ and $S$ the interaction is simply given by

$$\mathcal{H}_{LS} = \lambda L \cdot S$$

This is the spin orbit coupling. Generally, the crystalline field 'quenches the orbital angular momentum. In the special case of $3d^5$-ions (Mn$^{++}$, Fe$^{3+}$) the spectroscopic state is $^6S_{5/2}$ giving $L = 0$. Hence, the spin orbit coupling vanishes. However, higher order calculations in perturbation theory (that is, mixing of excited states)
yields non-zero values for the energy.

The form of the spin Hamiltonian of an ion depends on the symmetry of its surroundings as well as on the magnitude of its spin. For many compounds the environment of the ions is primarily cubic consisting of 4 or 6 almost equidistant anions. The departure from cubic symmetry is usually axial in nature, although there may be terms of lower symmetry. These non-axial terms are neglected here. With this approximation the most general spin Hamiltonian for a spin $S \leq 5/2$ is (Abragam and Pryce, 1951)

$$
\mathcal{H} = g_{\mu_B} S \cdot B + \frac{1}{6} a (S_x^4 + S_y^4 + S_z^4) + D S^2_\alpha + f S_\alpha^4 \quad (1.4.2)
$$

where $\alpha$ denotes the direction of the axial distortion.

For paramagnetic salts $D$ is often considerably larger than $a$, while $f$ is negligibly small. The first term in $\mathcal{H}$, which in the paramagnetic case represents the effect of an applied field, in the case of a magnetic material represents the exchange interaction of the ion with its magnetic neighbours. Van Vleck and Penney (1934) obtain the quartic term in $\mathcal{H}$ by fifth order perturbation theory involving the octahedral crystal field to the first power and $\lambda$ to the fourth power. The $S_\alpha^2$ term can be obtained in fourth order perturbation theory involving $\lambda$, as well
as from configuration interactions within the ion which
cause small departure of the electron cloud from spherical
symmetry (Abragam and Pryce, 1951). Note that, although
a term in $S_a^2$ is present, $g$ is very often effectively
isotropic. If the anisotropic Hamiltonian is given by the
$D$ and $a$ terms in $\mathcal{H}$ denoted above, the anisotropic
contribution to the free energy of the material is
(Kanamori, 1963) to first order, assuming the axial
anisotropy lies along the z-axis of the octahedral
symmetry (and ignoring constant terms),

$$F_a = -\frac{15}{4} [(D-2a)\cos^2 \theta + 2a \cos^4 \theta],$$  \ \ (1.4.3)

where $\theta$ is the angle the spin makes with the z-axis.
The coefficients of $\cos^2 \theta$ and $\cos^4 \theta$ are known respectively
as the first and second single-ion anisotropy.

The interionic dipolar interaction between
spins $S_i$, $S_j$ is given by

$$\mathcal{J} d = \frac{(g_\mu_B)^2}{3} \left[ S_i \cdot S_j - 3(S_i \cdot r_{ij})(S_j \cdot r_{ij})/r_{ij}^2 \right]$$

where $r_{ij}$ is the vector joining $S_i$ and $S_j$. This term gives
rise to an anisotropy energy to first order. When spin-
orbit coupling is not neglected in the calculation of the
exchange energy a term similar to the dipolar term arises
(Van Vleck, 1937; Tessman, 1954). This interaction arises
in second order perturbation theory and is given by

\[ pd = J \left( \frac{\lambda}{\Delta E} \right)^2 \left[ S_i \cdot S_j - 3 \left( S_i \cdot r_{ij} \right) \left( S_j \cdot r_{ij} \right) / r_{ij}^2 \right] \]

where \( \lambda \) is the spin-orbit coupling, \( \Delta E \) is the energy difference between the ground and excited states of the orbital levels and \( J \) is the exchange coupling. This coupling is called pseudo-dipolar. The net effect of the dipolar and pseudo-dipolar interactions is called the anisotropic exchange and is usually simply given by

\[ \mathcal{H}_K = K \sum_{ij} S_{iz} S_{jz} \]

1.5 Contact Cooling

The cooling mechanisms of a specimen of MnCl\(_2 \cdot 4\)H\(_2\)O are shown schematically in figure 1.4. At temperatures below 200 mK the dominant heat capacity of the system is that of the naturally abundant \(^{55}\)Mn nuclear spins. The spin lattice relaxation times for the \(^{55}\)Mn and \(^{54}\)Mn systems are not known and could differ greatly (as discussed in section 1.3E). The lattice is cooled by contact with a copper heat sink through a grease. The heat is conducted from the specimen to the contact material by phonons. Little (1959) has given the theoretical formula

\[ \dot{Q} = KA(T_1^4 - T_2^4) \]  

(1.5.1)
Figure 1.4 Schematic diagram of the cooling of MnCl$_2$·4H$_2$O.
where $A$ is the contact area and $T_1$ and $T_2$ give the temperature of the lattice and contact material) for a chrome alum to copper interface. Experimental observations (Anderson et al., 1961) for this situation confirm the $T^4$ relation and give the constant as

$$K = 6.2 \times 10^4 \text{ erg sec}^{-1} \text{K}^{-4} \text{cm}^{-2}$$

Empirical observations have been made assuming

$$Q = (T^n - T_0^n)$$  \hspace{1cm} (1.5.2)

for contact between materials at low temperatures. Some of these results have been given by Vilches and Wheatley (1966). A similar result might be expected for the MnCl$_2$·4H$_2$O to copper contact.

Assuming equal lattice and nuclear temperatures, the cooling of the specimen is given by the following equation

$$\dot{Q} = C_N \dot{T} + \dot{q}$$

where $\dot{Q}$ is the heat loss through the contact, $\dot{q}$ is the heat leak into the specimen and $C_N$ is the nuclear heat capacity. Using equation (1.5.2) gives

$$K \dot{A} (T^n - T_c^n) = -C_N \dot{T} + \dot{q}$$  \hspace{1cm} (1.5.3)
The ultimate temperature of the system, $T_0$, is given when $T=0$, hence

$$\dot{q} = KA(T_n^0 - T_C^n)$$  \hfill (1.5.4)

The nuclear heat capacity is given by

$$C_N = C_0/T^2$$  \hfill (1.5.5)

Combining equations (1.5.3) to (1.5.5) yields,

$$-\frac{\dot{T}}{T^2} = \frac{KA}{C_0} (T^n - T_0^n)$$  \hfill (1.5.6)

This equation can be used to determine the thermal conductivity constant $K$ of the contact if the specimen cooling has been determined.
CHAPTER II
The Experimental Procedures

2.1 Growth of the Crystal Specimens

Crystal specimens of MnCl$_2$·4H$_2$O were grown by evaporation from the saturated solution. Initially they were grown on hairs in a constant temperature bath. However, the following simpler method produced crystals of good quality.

A saturated solution of 10 ml of MnCl$_2$·4H$_2$O containing about 200 $\mu$Ci of carrier-free $^{54}$Mn was prepared. This solution was poured into a warmed evaporating dish to a depth of about 1 cm. A drop of hot water was added to the solution and stirred in so that a slightly under-saturated solution, with no seeds, was obtained. A small seed crystal (of about 3 mm$^3$ volume) was placed in the solution on the bottom of the evaporating dish. The container was then covered with a filter paper and left at room temperature for about two days in which time the crystal had grown to about 1 cm in length. The crystal was then removed from the solution and stored. Crystals of MnCl$_2$·4H$_2$O of dimensions of about 1 cm x 1 cm x 0.3 cm and having an activity of about 25 $\mu$Ci were obtained. The
crystallographic axes of the specimens were readily
determined by inspection of the crystal faces (Groth, 1908).

2.2 The Cryostat and the Crystal Holder

The low temperatures required for the experiments
were achieved by demagnetization of a paramagnetic salt.
A schematic diagram of the cryostat is shown in figure 2.1.
The paramagnetic salt used was chrome potassium alum.
Embedded in the alum were approximately 5000 copper wires
having a combined surface area of about 2000 cm². These
wires were soldered into a copper cold finger to which
the crystal holder (described below) was attached. A
⁶⁰Co-Fe plate was also soldered to the copper cold finger
to provide a low temperature nuclear orientation thermometer
(Campbell et al. 1965). A copper heat shield enclosing the
chrome alum pill and cold finger was cooled by a manganous
ammonium sulphate 'guard' pill. A jacket cooled by a 1K
pumped liquid helium bath enclosed the entire salt pill
assembly. An outer 4K liquid helium bath contained three
superconducting solenoids. Two of the superconducting
solenoids, producing fields of 35 KG and 10 KG, were used
to demagnetize the chrome alum pill and the guard pill
respectively. With this cryostat the temperature of the
cold finger, as measured by the nuclear orientation thermo-
Figure 2.1 The Cryostat.
meter, was less than 20 mK for a period exceeding 48 hours. Magnetic fields were applied to the specimen by a superconducting solenoid having a maximum field of 15 KG and an inhomogeneity of less than 1% over a sphere of 1.5 cm diameter.

To achieve optimum heat transfer from the crystal specimen to the copper cold finger by contact cooling it was necessary to utilize as much contact area as possible. Furthermore, a covering over the crystal would prevent heating caused by the adsorption of any residual exchange gas. Therefore, the crystal was mounted in a copper holder which had been soft-soldered to the copper cold finger. The crystal holder was made of copper foil (1/64 inches thick) folded to fit the crystal.

The crystal was mounted in the holder using Apiezon N grease for thermal contact. The crystal planes and edges were in contact with the planes and edges of the holder so that the latter served to orient the crystal. Good contact to the crystal was obtained by tying thread tightly around the holder.

A crystal holder was not used for the NMR-ON experiments because it would have attenuated the applied radio-frequency field. In this case, the crystal was simply fastened to the heat sink with Apiezon N grease and
thread. For the susceptibility measurements the crystal was inserted in a secondary coil which served as the crystal holder and which was glued with GE 7031 varnish to the copper cold finger.

In order to determine the directions of the sub-lattice magnetizations relative to the crystal axes of the mounted specimen it was necessary to know the crystal orientation in the frame of reference of the detectors, that is, the laboratory frame. This measurement was facilitated by temporarily mounting a small mirror on the crystal or crystal holder. A laser light and mirrors mounted on the laboratory walls were then used to determine the specimen orientation in the laboratory frame.

2.3 Gamma-Ray Detectors and Spectrum Analysis

The nuclear orientation experiments were performed using from two to four detectors at a time. These detectors were positioned to optimize the information obtained. The detector orientations relative to the crystal position were determined in the laboratory frame of reference. The gamma radiation intensity was measured with both NaI and Ge(Li) detectors. The NaI crystals were 2" diameter by 2" length. The two Ge(Li) detectors used in the experiments had efficiencies of 6% and 13% compared to a 3" x 3" NaI
crystal. The outputs of the detectors were amplified and routed to a multi-channel analyser which accumulated the spectra. In addition selected gamma-ray peaks were monitored through single channel analysers and scalers. After each counting period the analyser spectra were punched out on paper tape which was read into the University's IBM 370/168 computer for analysis.

The gamma-ray spectra contained one $^{54}$Mn peak at 0.837 MeV and two $^{60}$Co peaks at 1.17 and 1.33 MeV. The photopeak intensities were determined by subtracting a background count from the total number of counts in a 'window' set on the photo-peak. The 'background count' was determined by measuring the counts on each side of the peak and interpolating. In this manner, true background from degraded $^{60}$Co radiation and some actual $^{54}$Mn peak radiation was included in the background correction. The assumption that the background is linear is better for a Ge(Li) detector than a NaI detector. Nevertheless, since only relative intensities are required in this work, this background correction was found to be satisfactory. Indeed, in the case of the NaI detectors, it was found that the anisotropy of the estimated background on the $^{54}$Mn peak was almost equal to the $^{54}$Mn peak anisotropy indicating that the true background made only a small contribution.

The analysis of the approximately 100 spectra per
run was done using computer programs. All of the spectra in the run were analysed using the same window which was corrected for any shifts in peak position. The normalized intensity $W$ (equation 1.1.1) for each detector was obtained by dividing the cold count by the average 'warm count' for that detector. The warm counts were obtained with the specimen at sufficiently high temperature ($\geq 1$K) that the anisotropy of the radiation was negligible.

For some of the shorter counting periods scaler counts were taken without the analyser counts (because of the long printout time required by the analyser). In this case, the scaler windows and counts were periodically checked against analyser spectra to determine whether any shifts had occurred. If required, a subsequent renormalization of scaler counts could be performed.

2.4 Analysis of Anisotropies

As discussed in section 1.1, the angular distribution can be analysed to determine the orientation of the spin systems and their temperature. It requires two angles to locate a direction in space so that in order to determine two sublattice directions and the temperature as well, it is necessary to have at least five independent measurements of the anisotropy, that is, five measurements
at different angular positions. Four detectors were available for these experiments and this was the maximum number used. Also, four detectors gave a counting system which was not overly complex. In practice, because certain physical assumptions could be made, adequate information was obtained with this number of detectors.

All the observed anisotropies for a given applied field will represent the same magnetic configuration in the specimen. A gamma-ray intensity measured on a detector located in direction \( \mathbf{D}_i \) for a specimen temperature \( T_j \) is designated \( W_{ij}^{\text{ex}} \). Theoretical intensities \( W_{ij}^{\text{th}}(\{V_k\}) \) can be determined for any set of variables \( \{V_k\} \) such as the sublattice orientations and the temperature. The \( W_{ij}^{\text{th}} \) intensities can therefore be fitted to the \( W_{ij}^{\text{ex}} \) to determine the desired variables. The best fit was determined by minimizing chi squared:

\[
\chi^2 = \sum_{i,j} \left( \frac{W_{ij}^{\text{th}} - W_{ij}^{\text{ex}}}{\varepsilon_{ij}} \right)^2
\]

where \( \varepsilon_{ij} \) is the estimated standard deviation in the anisotropies. Included in the standard deviation \( \varepsilon_{ij} \) is the uncertainty in the detector position. If the detector \( i \) has its position specified by the angles \( \theta_i, \phi_i \), then

\[
\varepsilon_{ij}^2 = \left( \frac{\partial W_{ij}^{\text{th}}}{\partial \theta_i} \right)^2 \varepsilon^2(\theta_i) + \left( \frac{\partial W_{ij}^{\text{th}}}{\partial \phi_i} \right)^2 \varepsilon^2(\phi_i) + \delta^2
\]
where $e(\chi)$ indicates the uncertainty in $\chi$, and $\delta$ is the standard deviation in the count rate.

The accuracy of the solution was determined numerically. For any variable of the solution, $V_k$, the error is given by

$$e^2(V_k) = \sum_{i,j} (\partial V_k / \partial P_j)^2 e^2(P_j),$$

where the $P_j$ are all the input parameters such as the observed anisotropies and the detector positions. The partial derivatives $(\partial V_k / \partial P_j)$ were calculated by incrementing each parameter and determining the change in the variables in the resultant best fit.

2.5 Description of an Experimental Run

After the MnCl$_2$•4H$_2$O specimen was mounted and the demagnetization cryostat assembled, the cryostat was precooled with liquid nitrogen contained in an outer dewar. Liquid helium was transferred into the cryostat and the 1K bath. The salt pill assembly was kept in thermal contact with the liquid helium by helium exchange gas. When the system had cooled to liquid helium temperature the initial 'warm' (normalization) gamma-ray counts were taken after which the superconducting demagnetization solenoids were charged to magnetize the salt pills. The liquid helium in
the 1K bath was pumped to cool the bath. During this period thermal contact was maintained between the salt pills and the 1K bath by exchange gas at a pressure of 20 mtorr. When the temperature of the salt pill assembly and 1K bath had fallen to approximately 1.1K the salt pill assembly was thermally isolated by pumping away the exchange gas. The superconducting solenoids were demagnetized over about 5 minutes thereby cooling the salt pill assembly. The MnCl$_2$·4H$_2$O specimen cooled to very low temperatures (<150 mK) within one hour. The nuclear orientation experiments were performed by applying magnetic fields to the specimen while accumulating data from the gamma-ray detectors. After these experiments were completed the specimen and salt pill assembly were warmed to the temperature of the 1K bath and additional warm counts were taken.

2.6 The Experiments

In this section a brief description of the various runs will be given. The detector and crystal orientations are given in table 2.1. The crystal parameters are given in table 2.2.
# TABLE 2.1

Detector Orientations

The detector and applied fields are given in the crystal (a*, b, c) coordinate system using polar coordinates in degrees.

<table>
<thead>
<tr>
<th>Run</th>
<th>Detector number</th>
<th>Detector Position</th>
<th>Applied Field</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \theta )</td>
<td>( \phi )</td>
</tr>
<tr>
<td>A</td>
<td>1</td>
<td>85</td>
<td>-20</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>107</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>179</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>96</td>
<td>195</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>89</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>87</td>
<td>-48</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>179</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>90</td>
<td>14</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>90</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>90</td>
<td>-17</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>180</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>160°</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>190°</td>
<td>0</td>
</tr>
</tbody>
</table>

The accuracy of all angles quoted is typically ±3°.
## TABLE 2.2

### Crystal Parameters

<table>
<thead>
<tr>
<th>Run</th>
<th>A and B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimensions (cm) (along a*,b,c axes)</td>
<td>1.5x.89x.34</td>
<td>1.6 long.</td>
<td>1.21x.70x.30</td>
</tr>
<tr>
<td>activity (µCi)</td>
<td>24 ± 1</td>
<td>15 ± 1</td>
<td>24 ± 1</td>
</tr>
<tr>
<td>mass (gm)</td>
<td>0.39 ± .005</td>
<td>0.3 ± 0.1</td>
<td>0.39 ± .005</td>
</tr>
<tr>
<td>contact area (cm²)</td>
<td>1.7 ± 0.1</td>
<td>3.0 ± .5</td>
<td>1.1 ± 0.1</td>
</tr>
</tbody>
</table>
2.6i The Nuclear Orientation Experiments

Runs A and B were performed on the same specimen of MnCl$_2$·4H$_2$O. However, the magnetic field orientation and the detector positions relative to the crystal axes were different in each run. For run A the crystal was aligned so that the magnetic field was 5 degrees from the c-axis towards the c*-axis; for run B the crystal was aligned with the c-axis along the applied field. Comparison of the results of these runs for applied fields in the spin-flop transition region would give information on the dependence of the transition to small changes in magnetic field alignment.

The typical variation of the normalized intensities for applied fields in the spin-flop transition region is shown in figure 2.2 for run B. Data from two detectors is shown. One detector was aligned along the crystal c-axis, the other was in the a*-b plane. The field was first swept up, then down through the transition. It may be noted that the final anisotropies at the end of the sweep down are greater in magnitude than the initial values at the beginning of the sweep up. This effect results from the cooling of the specimen during the period of measurement (about two hours).

Run C was performed with the crystal c-axis aligned
Figure 2.2  Field Sweep through the Spin-Flop Transition. The lines shown are smooth curves drawn through the data points. $W_{ax}$, $W_{eq}$ are data for axial and equatorial detectors respectively.

+ field sweeping up.  0 field sweeping down.
along the applied field. Three detectors were used in the run. A different solenoid was used for the applied field in this run. Its field was calibrated by comparing the spin-flop transition with the other runs.

Run D was performed specifically to determine the direction of the sublattice magnetization in the a-c plane with no applied field. Only two detectors were needed; one was at $\theta = +10$ and the other at $\theta = -10$ in the a-c plane. Because an attempt was also to be made to observe NMR-ON of the $^{54}\text{Mn}$ nuclei no crystal holder was used in this run, the crystal being fixed directly to the copper cold finger. Consequently, the cooling of this specimen was not so efficient.

In these nuclear orientation runs about 350 gamma ray spectra were taken and about 10 magnetic field sweeps through the spin flop transition were made. The time required to perform a single low temperature run was about 36 hours.

2.6ii The Nuclear Magnetic Resonance Experiment

The radio-frequency (r.f.) field was applied to the crystal by a single turn coil. The coil was attached outside the 1K jacket which was fitted with a glass tail. The r.f. field strength at the crystal was rather inhomogeneous varying from 10 to 30 mG. The coil was oriented to direct
the field along the a*-axis.

The r.f. field was frequency modulated at 1 MHz bandwidth with a 10 Hz modulation frequency. The frequency of the r.f. field was swept over a range encompassing the expected resonance frequency of the $^{54}$Mn nuclear spins in MnCl$_2$·4H$_2$O which had been determined from a measurement of the hyperfine interaction (Miedema et al., 1965) to be 542 ± 10 MHz. The frequencies from 530 MHz to 550 MHz were swept at about 0.3 MHz/min. A broader range of 510 to 530 MHz and 550 to 570 MHz was swept at 1 MHz/min.

Two gamma-ray detectors were used. The temperature of the crystal and the $^{60}$Co-Fe plate on the cold finger were deduced from the anisotropies of the $^{54}$Mn and $^{60}$Co gamma-rays. A Ge(Li) detector positioned in the equatorial plane along the a*-axis was employed for these measurements. In order to detect the nuclear magnetic resonance, a large detector efficiency was desired. To this end a NaI detector with a large crystal of size 5 inches by 4 inches was used to monitor the intensity of the $^{54}$Mn radiation. It was mounted axially along the crystal c-axis.

The size of the equilibrium anisotropy observed on the NaI detector was 7%. The count rate was $2 \times 10^3$ counts per second giving an accuracy of ±0.2% in a 100 second interval. The count rate was monitored with a rate-meter and with a multichannel analyser in the multiscaling
mode. Surprisingly, no significant variations from equilibrium were observed in this experiment.

2.6iii Susceptibility Measurements

The spin-flop transition in MnCl$_2$·4H$_2$O was also determined from the field dependence of the parallel susceptibility. A mutual inductance technique was used for these measurements. One half of the secondary pick-up coil was wound on the specimen with its axis parallel to the c-axis of the crystal. The coil was mounted on the heat sink parallel to the applied field. The second half of the secondary was an identical coil wound in the opposite sense and mounted on the other side of the heat sink. Each coil had 500 turns of number 40 AWS copper wire and dimensions of 1.0 cm x 0.94 cm x 0.3 cm. The crystal was inserted in its coil with Apiezon N grease and both coils were glued to the heat sink with GE 7031 varnish. The primary coil was wound on a nylon tip at the bottom end of the heat shield. The signal frequency used was 42 KHz.

The secondary voltage was monitored by a lock-in amplifier with a 10 MΩ input impedance preamplifier. The susceptibility was measured for applied fields from 0 to 10 KGAuss.
The susceptibility of the specimen was determined as a function of temperature. For temperatures in the region accessible by pumping liquid helium the temperature was given by the helium vapour pressure. For temperatures of about 1/3 K an incomplete demagnetization was performed. For an adiabatic demagnetization the final and initial temperature $T$, $T_i$ respectively and the final and initial fields $H$, $H_i$ are related by

$$\frac{T}{T_i} = \frac{H}{H_i} \quad \text{for } H >> 100 \text{ G}$$

Therefore, the final equilibrium temperature is simply dependent on the final field and the initial conditions. In the actual experiment the initial temperature and field were 1.09 K and 32.3 KG whereas the final field was 8.80 KG resulting in a final temperature of 0.30 K. The specimen felt some 'stray' field from the demagnetization solenoid. The size of this stray field was determined by the change in the spin-flop transition point in fields applied in opposite directions. Its magnitude was 0.506 KG. Very low temperatures ($\sim 100$ mK) were achieved by complete demagnetization. In this case the temperature was measured by the nuclear orientation of the $^{54}$Mn in the specimen.
2.7 The Internal Field Calculation

The internal field in an ellipsoid magnetized along one of its axes is given by

\[ H_{\text{int}} = H_{\text{applied}} - DM, \]

where \( D \) is the demagnetizing factor which is dependent on the specimen geometry, and \( M \) is the magnetization. \( DM \) is called the demagnetization field. Chikazumi (1964) gives an equation for the demagnetization factor of an ellipsoid having dimensions \( a, b, c \) along its axes with \( a>b>>c \) and with the field applied along the \( c \)-axis.

\[ D = \left( \frac{4\pi}{4a} \right) \left[ \frac{1-\frac{3}{10}}{\frac{3}{4}} \left( \frac{a-b}{a} \right)^2 \right] \]

where \( D \) is in cgs units. In general, \( D \) is a tensor. In order to obtain an estimate of the average internal field, the crystal shape can be approximated to an ellipsoid and the above equation used to determine \( D \). For the susceptibility specimen (run D) the resultant value of the estimated demagnetization factor is \( D = 2.3 \) dgs units. A crystal which is not ellipsoidal will have a spatial variation of demagnetizing fields resulting in an increased width of the spin-flop transition.

In order to determine the internal field it is
necessary to know the magnetization $M$. This can be determined by integrating the susceptibility. However, the susceptibility measured in the experiments was in arbitrary units so that integration gives

$$M(H) = k \int_0^H \chi(H) \, dH$$

where $k$ is a normalization constant which must be determined. The nuclear orientation measurement of the spin direction in the spin-flop phase can also be used to determine the magnetization:

$$M(H) = 2M_o \cos \theta(H)$$

where $M_o$ is the sublattice magnetization

$$M_o = \frac{1}{2} g \mu_B S N$$

and $\theta$ is the angle between the spin directions and the field direction. The magnetization was determined from the results of section 3.2 to be $96 \pm 6 \text{ erg G}^{-1}\text{cm}^{-3}$ for $H_{\text{applied}} = 7.7 \text{ KOe}$. This is in good agreement with the value of $100 \pm 2 \text{ erg G}^{-1}\text{cm}^{-3}$ deduced from the results of Rives and Benedict (1975). The normalization $k$ in equation 2.7.1 can therefore be determined and the magnetization for any field can be calculated from the integral of the susceptibility curve.
CHAPTER III

Results

The nuclear orientation experiments have been analysed to determine the magnetic structure of the crystal. Models have been used which assume that the lattice of magnetic ion spins can be divided into a few sublattices in each of which the ionic spins are oriented in the same direction. The orientation of a sublattice spin relative to the orthogonal crystal lattice axes $a^*, b, c$ is defined by the polar coordinates $\theta, \phi$ where the polar angle $\theta$ is the angle between the spins and the $c$-axis, and the angle $\phi$ is the angle between the projection of the spins on the $a^*-b$ plane and the $a^*$-axis. The spin configuration is then specified by the polar coordinates $\theta, \phi$ for all the sublattices. This specification of the spin configuration is used throughout this chapter.

3.1 Spin Configurations in the Antiferromagnetic State ($H < H_{th}$)

The nuclear orientation experiments in which the applied field was less than the spin flop transition field have been analysed using a model for the spins, appropriate to $T=0$ in which there are two equal antiparallel sublattices.
In this case the total spin configuration is given by only two angles

\[ \theta = \theta_1 = \theta_2 - 180^\circ \]
\[ \phi = \phi_1 = \phi_2 \]

In runs A and B, in which four detectors were used, \( \theta, \phi \) and the temperature \( T \) were determined by solving (using computer analysis) the simultaneous equations for the anisotropy at each detector. For run C, in which only two detectors were used only the one angle \( \theta \) and the temperature were determined.

The results of the analysis of data taken with no applied field on the specimen are given in table 3.1. The quoted error includes the statistical error in the radiation intensity and the error in the alignment of the crystal and detectors. The average value for the spin direction is

\[ \theta = 11.5 \pm 3.5 \text{ deg.}; \phi = 10.5 \pm 5.0 \text{ deg.} \]

These results agree quite well with measurements of Altman et al. (1975) who obtained the more accurate result of

\[ \theta = 6.9 \pm 2.0 \text{ deg.}; \phi = 2 \pm 2 \text{ deg.} \] by three dimensional neutron scattering. The combined result gives

\[ \theta = 7.6 \pm 1.6 \text{ deg.}; \phi = 3.2 \pm 1.9 \text{ deg.} \]
TABLE 3.1

Spin Configurations Without Applied Field

<table>
<thead>
<tr>
<th>Run</th>
<th>θ</th>
<th>ϕ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9.0 ± 6.4</td>
<td>7.5 ± 7.2</td>
</tr>
<tr>
<td>B</td>
<td>14.5 ± 6.4</td>
<td>18.0 ± 7.2</td>
</tr>
<tr>
<td>C</td>
<td>12.3 ± 8.0</td>
<td>-30 ± 20</td>
</tr>
<tr>
<td>D</td>
<td>11.0 ± 5.0</td>
<td>0.0&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Averages  θ = 11.5° ± 3.5°  
ϕ = 10.5 ± 5.0°

<sup>a</sup> run D measured projection of spin in a-c plane
The spin configurations for applied fields less than the spin flop transition field \( (H_{th}) \) and in the a-c plane were also determined using the same model. The results are given in table 3.2. In run A the field direction was between the c and c*-axis; in run B the field was along the c-axis. For both runs the analysis shows that within experimental error the spin configuration remained unchanged from the zero field configuration for fields up to 97% of the spin flop transition. In molecular field theory the spin configuration does not change for fields less than the spin-flop field if the applied field is along the easy axis. For a field inclined at an angle of 7° to the easy axis the theory predicts a maximum change \( \Delta \theta \) in the polar angles of the sublattices of less than 3°. This value of \( \Delta \theta \) was less than the uncertainties in the observed polar angles so that no changes in the spin configuration were expected. The spin configurations for applied fields in the region of the spin flop transition field will be discussed in section 3.4.

### 3.2 The Spin-Flop State

The nuclear orientation anisotropies for applied fields greater than the transition field were fitted to a model in which two equal sublattices were again assumed. If the field \( H \) is applied along the anisotropy axis both the
### TABLE 3.2

Field Dependence of the Spin Configuration in the Antiferromagnetic Phase

<table>
<thead>
<tr>
<th>$H_{\text{applied}}$</th>
<th>$\theta$</th>
<th>$\phi$</th>
<th>Run</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.19</td>
<td>$3.0 \pm 6.5$</td>
<td>$20 \pm 40$</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>$10.0 \pm 7.0$</td>
<td>$22 \pm 15$</td>
<td>B</td>
</tr>
<tr>
<td>6.061</td>
<td>$11.0 \pm 6.5$</td>
<td>$12 \pm 10$</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>$11.0 \pm 7.0$</td>
<td>$19 \pm 15$</td>
<td>B</td>
</tr>
<tr>
<td>6.79</td>
<td>$16 \pm 10$</td>
<td>$-20 \pm 22$</td>
<td>C</td>
</tr>
<tr>
<td>7.018</td>
<td>$5.0 \pm 5.0$</td>
<td>$0 \pm 25$</td>
<td>A</td>
</tr>
</tbody>
</table>
molecular field and the spin-wave models give a spin configuration in which the angles between \( H \) and the sublattice directions are equal and the projections of the sublattice directions in the plane perpendicular to \( H \) are antiparallel. Even if the applied field makes a small angle with respect to the anisotropy axis this description of the spin configuration is a good approximation to the molecular field result because of the small influence of the crystalline anisotropy terms in this region.

The gamma ray anisotropy data has been analysed using this model of the spin configuration to obtain the polar angle \( \theta \), and the angle \( \phi \) of the spin projections in the \( a^*-b \) plane with respect to the \( a^*-axis \), as well as the temperature of the spin system. The resultant spin configurations are given in table 3.3. The angle \( \phi \) which is not expected to depend on the applied field is \( \phi = 94 \pm 4 \) deg., indicating that the spins 'flop' into a plane very close to the \( b-c \) plane. These experimental results will be discussed in relation to the theoretical models in section 3.3.

3.3. The Molecular Field Values for \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \)

The molecular fields can be determined from the transition points. Rives and Benedict (1975) used their measured values of the paramagnetic transition fields \( H_{px} \).
### Table 3.3

**Spin-Flop State Configuration**

<table>
<thead>
<tr>
<th>Run</th>
<th>$H$ (KG)</th>
<th>$\theta$ (deg)</th>
<th>$\phi$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.656</td>
<td>70.0 ± 1.2</td>
<td>94.0 ± 3.5</td>
</tr>
<tr>
<td></td>
<td>10.53</td>
<td>61.0 ± 1.2</td>
<td>95.0 ± 3.5</td>
</tr>
<tr>
<td></td>
<td>12.44</td>
<td>54.0 ± 1.6</td>
<td>96.0 ± 3.5</td>
</tr>
<tr>
<td></td>
<td>14.36</td>
<td>46.0 ± 1.2</td>
<td>95.0 ± 3.5</td>
</tr>
<tr>
<td>B</td>
<td>7.656</td>
<td>70.0 ± 1.1</td>
<td>93.8 ± 3.5</td>
</tr>
<tr>
<td></td>
<td>10.53</td>
<td>60.0 ± 1.9</td>
<td>93.8 ± 3.5</td>
</tr>
<tr>
<td></td>
<td>13.80</td>
<td>49.0 ± 3.8</td>
<td>103.8 ± 3.5</td>
</tr>
<tr>
<td>C</td>
<td>7.89</td>
<td>72 ± 6</td>
<td>89 ± 5</td>
</tr>
<tr>
<td></td>
<td>10.08</td>
<td>62 ± 3</td>
<td>81 ± 5</td>
</tr>
</tbody>
</table>
\( H_{py} \), \( H_{pz} \) to obtain the values

\[
\begin{align*}
H_E & = 10.375 \pm 0.03 \text{ KOe} \\
H_{Kly} & = 2.20 \pm 0.05 \text{ KOe} \\
H_{Klx} & = 3.80 \pm 0.05 \text{ KOe}
\end{align*}
\]

These molecular fields can be used to determine the thermodynamic spin flop transition field \( H_{th} \) from the molecular field theory equation (section 1.2B):

\[
H_{th}^2 = 2H_E H_{Klx} - H_{Kly}^2
\]

giving \( H_{th} = 6.4 \pm 0.1 \text{ KOe} \). This value of \( H_{th} \) is in poor agreement with the observed value for the spin flop transition field of 7.0 KOe.

Our nuclear orientation results for the field dependence of \( \cos \theta \) in the spin flop state and the spin flop transition field can be used to determine \( H_E \) and \( H_{Kl} \) provided second order anisotropy and anisotropic exchange are both negligible. Using the relations (section 1.2B)

\[
\begin{align*}
H_{th}^2 & = 2H_E H_{Kl} - H_{Kl}^2 \\
\cos \theta & = H/(2H_E - H_{Kl})
\end{align*}
\]

the results are

\[
\begin{align*}
H_E & = 11.88 \pm 0.42 \text{ KOe} \\
H_{Kl} & = 2.31 \pm 0.04 \text{ KOe}
\end{align*}
\]
These values are in poor agreement with those deduced from the observed paramagnetic transition fields. For example, the calculated value of $H_{pz}$ is $21.45 \pm 0.42$ K.Oe whereas the value observed by Rives and Benedict is $18.55 \pm 0.05$ K.Oe.

Agreement between the transition points and the field dependence of $\cos\theta$ in the spin flop state can be obtained in the molecular field model if second order anisotropy is included. Anisotropic exchange is also included in the analysis. In this case the field dependence of the spin configuration $\cos\theta(H)$ is given by (section 1.2B)

$$\cos\theta = \frac{H}{H_0 - 2H_{K2} \cos^2 \theta} \quad (3.2.1)$$

where

$$H_0 = 2H_E + H_{KE} - H_{K1}.$$

The values $H_0 = 21.45 \pm 0.42$ K.Oe and $H_{K2} = 1.45 \pm 0.19$ K.Oe were obtained from 3.2.1 by a fitting procedure which utilized both the nuclear orientation data and the paramagnetic transition point $H_{pz}$. The data and the fitted curve are shown in figure 3.1.

The maximum deviation from linearity of $\cos\theta(H)$ is $5.6 \pm 0.8$ percent of the value of $\cos\theta_H$ at $H_{pz}$. A deviation from linearity for fields applied along the easy axis is also indicated in the magnetization measurements of Rives and Benedict. The maximum deviation for their results was $6.4 \pm 0.5$ percent of the magnetization at $H_{pz}$. However, the non-linearity
Figure 3.1  Polar Angle in the Spin-Flop Phase.

x Run A  0 Run B  △ Run C  ▽ H_{pz}
in the magnetization also includes a contribution from the field dependence of the sublattice magnetization arising from spin wave effects (section 1.2D). This contribution has been estimated to be only 2.4% (Miedema et al., 1965), leaving about 4.4% non-linearity which is in agreement with the nuclear orientation result.

The molecular fields can be determined from the transition fields given in section 1.2B:

\[ H_{py} = 2H_E + H_{kly} + H_{KE}; \quad H_{px} = 2H_E + H_{k lx} + H_{KE} \]
\[ H_{th} = \left[ H_0 (H_{kly} + H_{K2} + H_{KE}) \right]^{1/2} \]

The following fields are obtained:

\[ H_E = 11.05 \pm 0.21 \text{ KOe}, \]
\[ H_{KE} = 0.1 \pm 0.3 \text{ KOe}, \]
\[ H_{kly} = 0.75 \pm 0.22 \text{ KOe}, \quad H_{k lx} = 2.35 \pm 0.23 \text{ KOe}, \]
\[ H_{K2} = 1.45 \pm 0.19 \text{ KOe}, \]

as well as \( H_{KE} + H_{kly} = 0.86 \pm 0.20 \text{ KOe}. \)

These results indicate that the anisotropic exchange field \( H_{KE} \) is negligible which is not surprising since the \( g \)-factor for the \( ^6S \) state is isotropic \( (g = 2.0) \). The results also suggest that the second order anisotropy field is approximately twice the first order field. The second order anisotropy can arise from the (nearly regular) octahedral
arrangement of the two chlorine ions and four water molecules around the manganese ion. A small axial distortion of the regular octahedron can contribute an additional first order anisotropy. Using equation 1.4.3 the axial symmetry coefficient $D$ and the octahedral symmetry coefficient $a$ can be calculated for this system:

$$D = 0.96 \pm 0.15 \text{ cm}^{-1}; \quad a = 0.45 \pm 0.06 \text{ cm}^{-1}$$

These values are rather larger than those estimated from paramagnetic resonance of Mn$^{++}$ in paramagnetic materials. Typical values given are

$$D \approx +0.2 \text{ cm}^{-1}, \quad a \approx 0.02 \text{ cm}^{-1}.$$  

Unfortunately, because the anisotropic interaction arises from the crystal field through spin-orbit coupling only in fourth or fifth order of perturbation theory (for the $^6S$ state), even rough estimates of the expected effect are difficult to obtain.

3.4 The Spin-Flop Transition Region

For applied fields in the spin-flop transition region, the molecular field model for two sublattices gives solutions for the spin configurations which allow the
polar angles $\theta_1$, $\theta_2$ of each sublattice to assume different, independent values while the projections of the sublattice spins in the $a^*\cdot b$ plane remain antiparallel. The angles $\theta_1$, $\theta_2$ and $\phi = \phi_1 = \phi_2$ for the spin configuration in the transition region were fitted to the nuclear orientation data from runs A and B. The specimen temperatures used for fitting the anisotropies were obtained from the cooling curve (figure 3.6). In fact, the temperatures could have been determined in the actual fitting procedure, but using the cooling curve data reduced the number of parameters and thereby increased the accuracy of the result. The spin configurations obtained by the analysis are given in table 3.4 and the polar angles are plotted in figure 3.2. The results indicate that in increasing field the spin configuration goes from an antiferromagnetic phase ($\theta_2 = \theta_1 + 180^\circ$) to a spin-flop phase ($\theta_2 = -\theta_1$) with no detectable intermediate phase. However, it is also apparent that within the spin-flop phase between fields of 7.25 and 7.45 KG the value of $\cos \theta$ decreases with increasing applied field contrary to the theoretical result that $\cos \theta$ is proportional to $H$. It was concluded that the two sublattice model was not appropriate in the transition region.

It has been proposed by Keffer (1973) and Chow (1974) that a mechanism exists in the spin-flop transition which gives rise in the crystal to regions ('domains') of antiferromagnetic phase and regions of spin-flop phase. Consequently,
**TABLE 3.4**

Spin Configuration in the Transition Region

Using the Two-sublattice Model

<table>
<thead>
<tr>
<th>Run</th>
<th>$H_{\text{applied}}$ (kG)</th>
<th>$\theta_1$ degrees</th>
<th>$\theta_2$ degrees</th>
<th>$\phi$ degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.12</td>
<td>4</td>
<td>-176</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>7.21</td>
<td>53</td>
<td>-15</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>7.273</td>
<td>-62</td>
<td>44</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>7.43</td>
<td>-78</td>
<td>71</td>
<td>95</td>
</tr>
<tr>
<td>B</td>
<td>7.21</td>
<td>-36</td>
<td>160</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>7.273</td>
<td>-49</td>
<td>35</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>7.34</td>
<td>-61</td>
<td>51</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>7.43</td>
<td>-59</td>
<td>82</td>
<td>98</td>
</tr>
</tbody>
</table>
Figure 3.2 Two Sublattice Model in the Transition Region.

x Run A  O Run B
the nuclear orientation data was fitted to a model in which a fraction $\delta$ of the specimen is in the spin-flop configuration and a fraction $(1-\delta)$ is in the antiferromagnetic configuration. It is assumed that a negligible part of the specimen is in a transitional phase between these two configurations. The intensity of radiation from the specimen at a detector located in a direction $\mathbf{D}$ is given by

$$W(\mathbf{D}) = (1-\delta)W_{af}(\mathbf{D}) + (\delta)W_{sf}(\mathbf{D})$$

where $W_{af}$ and $W_{sf}$ are the angular distributions from the pure antiferromagnetic and spin-flop phases respectively.

The data from runs A and B were fitted to the model to obtain the fraction $\delta$ of spins in the spin-flop state. The individual spin configurations in the mixed phase specimen were assumed to be the appropriate spin configurations from just below and just above the transition region. The values of $\delta$ which were obtained from the analysis and their applied fields are given in table 3.5. The random error in $\delta$ arising from uncertainty in the anisotropies, the detector positions and the temperatures is $\pm 0.03$ for all values of $\delta$. The error in $\delta$ arising from the uncertainty in the spin configuration of the domains (as determined above and below the transition region) is $\pm 0.03$ for all $\delta$. Therefore the total expected uncertainty in $\delta$ is $\pm 0.04$. The variation of $\delta$ across
### Table 3.5

Transition Region Using the Domain Model.

$\delta$ is the Fraction of Spins in Spin-flop Phase

<table>
<thead>
<tr>
<th>$H_{\text{applied}}$ (kG)</th>
<th>$\delta(\pm 0.04)$ Run A</th>
<th>$\delta(\pm 0.04)$ Run B</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.12</td>
<td>0.0</td>
<td>0.03</td>
</tr>
<tr>
<td>7.21</td>
<td>0.45</td>
<td>0.25</td>
</tr>
<tr>
<td>7.273</td>
<td>0.725</td>
<td>0.50</td>
</tr>
<tr>
<td>7.34</td>
<td>0.90</td>
<td>0.775</td>
</tr>
<tr>
<td>7.43</td>
<td>1.0</td>
<td>0.96</td>
</tr>
<tr>
<td>7.53</td>
<td>-</td>
<td>0.96</td>
</tr>
</tbody>
</table>
the transition is plotted in figure 3.3 for the two runs. In run B in which the applied field was inclined at 7° to the easy axis the transition occurs at a slightly (0.7%) higher field than in run A in which the inclination was only 2°. In fact, molecular field theory predicts a shift for the two sublattice models in agreement with the observed value. Using 80% of the range of \( \delta \) as an empirical measure of the width of the transition, the observed width is 0.19 ± 0.02 KOe in run A and 0.24 ± 0.02 KOe in run B. The inhomogeneity of the applied field on the specimen was estimated to be 1% or 0.07 KOe. There is an additional inhomogeneity in the \textit{internal} field arising from the inhomogeneity of the demagnetization field of the specimen. The average demagnetizing field just above the transition region was 0.23 KOe. Estimating a 20% variation in this field gives a total inhomogeneity of the internal field of only 0.11 KOe which indicates that the observed width does not fully arise from field inhomogeneity.

Keffer and Chow did not determine the ratio of the phase populations in the transition region; however, they did determine the stability boundaries. The lower boundary in increasing field is \( (H_1^-)^2 = H_E H_A + H_A^2 \), and in decreasing field is \( H_2^- = H_A^3 / H_A^4 \). The upper boundary is \( H^+ = 2H_E H_A + H_A^2 \). These results apply to single-ion anisotropy at \( T=0 \) with the field applied along the easy axis. When the molecular field
Figure 3.3 $\delta$ in the Transition Region. Solid lines indicate a smooth fit through the data points.
values given in section 3.3 are used in the above expressions, the stability boundaries are given by

\[ \frac{H_1}{H_{th}} = 0.83, \frac{H_2}{H_{th}} = 0.90, \frac{H^+}{H_{th}} = 1.12 \]

where \( H_{th} \) is the thermodynamic transition field. Thus the observed width of the spin-flop transition lies well within the theoretically allowed boundaries.

If the specimen is in the transition region of field the magnetization is given by

\[ M = \delta M_s \cos \theta_{sf} \]

where \( \theta_{sf} \) is the polar angle in the spin-flop phase and \( M_s \) is the saturation magnetization. Hence \( \delta \) and the magnetization should be proportional. \( \delta \) can be determined from the nuclear orientation data and \( M \) can be determined from the integral of the susceptibility \( \chi \). In figure 3.4 the integral of the susceptibility and \( \delta \) are plotted against the applied field. The same crystal alignment was used for the measurements of \( \chi \) and \( \delta \). \( \chi \) was determined at temperatures between 0.3 and 0.15 K whereas \( \delta \) was determined at temperatures between 0.06 and 0.08 K. The two graphs (figure 3.4) are similar although the susceptibility gives a wider transition of 0.35 KOe. This increased width of the transition is possibly caused by variation in \( \theta_{sf} \) in the transition region which was not considered in the nuclear orientation analysis.
Figure 3.4 The Magnetization and $\delta$ in the Transition Region. The integral of the susceptibility, $M$ (in arbitrary units), is shown by the solid curve. The circles give the experimental values of $\delta$. 
It is concluded that whereas the two sublattice molecular field models fail to describe adequately the nuclear orientation data, the domain model using mixed phases in the spin-flop transition region does give satisfactory agreement with experiment.

3.5 The Temperature Dependence of the Spin-Flop Transition Field

The temperature dependence of the spin-flop transition at temperatures between 0.1 and 1K was also obtained from the a.c. susceptibility measurements. The values obtained from these measurements for the critical fields at temperatures in the region of 0.1K, 0.3K and 1.0K are given in table 3.6 and figure 3.5. It is apparent from figure 3.5 that the transition field continues to decrease as the temperature is lowered from 0.3K to 0.1K. The lowest field for the spin-flop transition occurred at the internal field \( H_{th} = 6.98 \pm 0.03 \) at the temperature \( T=0.12K \).

Rives and Benedict (1975) also determined the temperature dependence of the spin-flop transition field. They fitted their results to the upper boundary of the antiferromagnetic phase (\( H^+ \)) using a relation calculated from spin-wave theory by Feder and Pytte (1968). The fitted temperature dependence of the transition field had a minimum at 0.3K, the lowest temperature they reached in their measurements. In
**TABLE 3.6**

Temperature Dependence of the Spin-Flop Field

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Applied Field (kG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.115 ± .01</td>
<td>7.630 ± .002</td>
</tr>
<tr>
<td>1.09 ± .01</td>
<td>7.587 ± .002</td>
</tr>
<tr>
<td>0.9 ± .05</td>
<td>7.579 ± .002</td>
</tr>
<tr>
<td>0.8 ± .05</td>
<td>7.551 ± .007</td>
</tr>
<tr>
<td>0.30 ± .01</td>
<td>7.30 ± .01</td>
</tr>
<tr>
<td>0.15 ± .02</td>
<td>7.252 ± .002</td>
</tr>
<tr>
<td>0.12 ± .01</td>
<td>7.25 ± .01</td>
</tr>
</tbody>
</table>
Figure 3.5 Temperature Dependence of the Spin-Flop Transition Field.
fact, in an antiferromagnet the actual transition does not occur at \( H^+ \) but at \( H_{th} \) (the thermodynamic transition point at which the free energies of the phases are equal). It is unlikely that \( H^+ \) and \( H_{th} \) would have the same temperature dependence so that the use of the Feder and Pytte theory by Rives and Benedict to extrapolate their data was not justified.

We conclude that any minimum in the temperature dependence of the spin-flop transition field must occur below 0.15K.

3.6 Cooling of the Specimens

Measurement of the gamma-ray anisotropy allows the determination of the temperature of the spin systems (in addition to the spin quantization directions). The actual parameters determined in the temperature analysis are the B coefficients in the expression for the anisotropy (equ. 1.1.1). The B coefficients are a function of \( \beta = \mu I H_{hf}/IKT \). Hence, determination of the B coefficients and previous knowledge of \( I, \mu I \) and \( H_{hf} \) yields the temperature of the system. The value of \( H_{hf} \) used in the calculation was determined by nuclear specific heat measurements. Spin wave effects result in a field dependence of the sublattice magnetization even at low temperatures. This field dependence is reflected in the average hyperfine field of the sublattice. However, the total change in
the sublattice magnetization has been estimated to be only 2.4% (Miedema et al., 1965). There was an additional change in $H_{hf}$ of not greater than 3% arising from the presence of the applied field. These variations in $H_{hf}$ were not significant in the determination of $T$ and were therefore ignored in the analysis.

In the experiments the specimen was cooled by the copper cold finger through Apiezon N grease. The temperature of the specimen as a function of time can be used to determine the thermal conductance $\dot{Q}/\Delta T$ of the contact. The temperature data of runs A and B, given in table 3.7, has been fitted to a relation of the form (section 1.5)

$$\dot{Q} = kA(T^n - T_0^n)$$

(3.6.1)

where $\dot{Q}$ is the heat flux, $T_0$ is the ultimate temperature, $A$ is the contact surface area and $k$ is a thermal conductivity constant for the contact. Assuming $n=4$, the best fit of the data gives the thermal conductivity constant:

$$k = (8.2 \pm 1.9) \times 10^3 \text{ erg K}^{-4} \text{ sec}^{-1} \text{ cm}^{-2},$$

and $T_0 = (47 \pm 5)$ mK.

The data fitted curve are shown in figure 3.6. The data was also fitted to the equation with $n=3$. In this case the conductivity constant is

$$k = (6.3 \pm 1.9) \times 10^2 \text{ erg K}^{-3} \text{ sec}^{-1} \text{ cm}^{-2}.$$
<table>
<thead>
<tr>
<th>Run A</th>
<th>end of demagnetization: ( t_0 = 1600 ) hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T ) (mK)</td>
<td>time ( \pm 1 ) min</td>
</tr>
<tr>
<td>150 ( \pm 30 )</td>
<td>1602</td>
</tr>
<tr>
<td>130</td>
<td>1610</td>
</tr>
<tr>
<td>123</td>
<td>1614</td>
</tr>
<tr>
<td>112 ( \pm 20 )</td>
<td>1617</td>
</tr>
<tr>
<td>145 ( \pm 30 )</td>
<td>1621</td>
</tr>
<tr>
<td>102</td>
<td>1626</td>
</tr>
<tr>
<td>102 ( \pm 15 )</td>
<td>1634</td>
</tr>
<tr>
<td>73 ( \pm 6 )</td>
<td>1734</td>
</tr>
<tr>
<td>65 ( \pm 5 )</td>
<td>1813</td>
</tr>
<tr>
<td>59</td>
<td>1921</td>
</tr>
<tr>
<td>58( \frac{1}{2} ) ( \pm 3 )</td>
<td>1942</td>
</tr>
<tr>
<td>53</td>
<td>2038</td>
</tr>
<tr>
<td>50</td>
<td>2140</td>
</tr>
</tbody>
</table>

cont'd...
TABLE 3.7 (continued)

Run B  end of demagnetization:  \( t_o = 1600 \) hours

<table>
<thead>
<tr>
<th>T (mK)</th>
<th>time (hours/min)</th>
<th>T (mK)</th>
<th>time (hours/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>115 ± 20</td>
<td>1608</td>
<td>62</td>
<td>1908</td>
</tr>
<tr>
<td>113</td>
<td>1612</td>
<td>63( \frac{1}{2} )</td>
<td>1949</td>
</tr>
<tr>
<td>137</td>
<td>1616</td>
<td>58</td>
<td>2119</td>
</tr>
<tr>
<td>100 ± 15</td>
<td>1623</td>
<td>51</td>
<td>2207</td>
</tr>
<tr>
<td>100</td>
<td>1627</td>
<td>57</td>
<td>2247</td>
</tr>
<tr>
<td>110</td>
<td>1631</td>
<td>54( \frac{1}{2} )</td>
<td>2342</td>
</tr>
<tr>
<td>86</td>
<td>1636</td>
<td>53</td>
<td>2420</td>
</tr>
<tr>
<td>80</td>
<td>1641</td>
<td>49 ± 2</td>
<td>2500</td>
</tr>
<tr>
<td>75 ± 4</td>
<td>1745</td>
<td>52( \frac{1}{2} )</td>
<td>2541</td>
</tr>
<tr>
<td>67</td>
<td>1824</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.6 Cooling of the Specimen.

x Run A     O Run B
with \( T_0 = (46 \pm 5) \text{ mK} \).

This fitted curve is also shown in figure 3.6. Both curves fit the data reasonably well.

According to the theory of Little (1959), the boundary resistance depends on the acoustic mismatch between the materials and is a function of their densities and acoustic velocities. It has been shown (Peterson et al., 1973; Allen, 1974) that, in addition to the scattering of phonons at the surface considered by Little, the scattering of phonons within the material should be considered in the analysis of the boundary resistance. Peterson et al. obtain good agreement with theory for a number of different contacts.

Metcalfe (1971) has observed effects in the thermal conductivity of \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \) which he associated with magnon-phonon scattering and which could be significant in the boundary resistance. Unfortunately, it is not possible with the present theoretical knowledge and the limited experimental data to determine quantitatively to effects of the various processes. Furthermore, in any individual measurement the contact resistance may be strongly effected by factors such as imperfect surface contact, imperfections in the surface layers at the interface, and surface strains due to differential contraction, all of which tend to increase the contact resistance. It is not surprising, therefore, that the conductivity constant \( k \) measured in the present case for
MnCl₂·4H₂O is an order of magnitude different than that observed for a contact of chrome potassium alum to copper with Apiezon N grease.

The spin-lattice relaxation time $T_1$ of the manganese nuclear spin system has so far been ignored in the analysis. In earlier work on MnCl₂·4H₂O at low temperatures (Daniels et al., 1961 and Miedema et al., 1965) the suggestion was made that the cooling rate was limited by the spin-lattice relaxation. Using the relation 3.6.1 for $n=4$ with the fitted values for $k$ and $T_0$, and assuming a temperature dependent time constant $T_1(T)$ defined by,

$$\frac{dT}{dt} = \frac{T-T_0}{T_1(T)}$$

gives relaxation times $T_1 = 3 \times 10^3$ s at $T = 100$ mK and $T_1 = 40 \times 10^3$ s at $T = 50$ mK. These values for $T_1$ represent the upper limit of the nuclear spin-lattice relaxation, assuming this contribution dominates the thermal resistance.

Perhaps in MnCl₂·4H₂O where the dominant contribution to the heat capacity is that of the nuclear spin system, the boundary resistance should ideally be treated in terms of the coupled systems of lattice, electronic and nuclear spins.
CHAPTER IV

Nuclear Orientation of $^{103}\text{Ru}$

4.1 Introduction

Anisotropic radiations from oriented nuclei can be used to determine information about the nuclear system being observed. As discussed in section 1.1, Blin-Stoyle and Grace (1957) show that the gamma-ray intensity, observed at angle $\theta$ to the axis of quantization, is given by

$$W(\theta) = \sum_{K \text{ even}} B_K U_K F_{K} F_{K'} (\cos \theta)$$  \hspace{1cm} (4.1)

The coefficients $B_K$, which are discussed in detail in section 1.1, describe the nuclear orientation of the initial system (preceding any nuclear decay). They are functions only of the initial nuclear spin $I_0$ and, in the case the hyperfine interaction can be described by a hyperfine field $H_{hf}$, $\beta = \nu H_{hf}/IKT$ where $\nu$ is the nuclear magnetic moment and $T$ is the temperature of the system. The coefficient, $F_K$, depends on the angular momentum properties of the observed transition. If a state of angular momentum $I_1$ decays to a state of angular momentum $I_2$ by emission of angular momentum $L$ the coefficient $F_K$ is
given by $F_K(\text{L1I2I1})$ for which the expression is

$$F_K(\text{L1I2I1}) = (-1)^{I_1-I} \left[ \frac{1}{2} \left( 2L+1 \right) \left( 2L'+1 \right) \left( 2I_1+1 \right) \right]^\frac{1}{2} \cdot C(\text{L1I2I1}; \text{L0I0I0}) W(I_1I_1; \text{KLI2})$$

where $W$ is a Racah coefficient. If the observed gamma transition has mixed multipolarity then the coefficient $F_K$ is given by

$$F_K = \left[ F_K(\text{L1I2I1}) + \delta^2 F_K(\text{L1I2I1}) + 2 F(\text{L1I2I1}) \right] / [1+\delta^2]$$

for a $2^L$ pole transition in which is admixed an amplitude $\delta$ of $2^{L+1}$ pole radiation. Clearly this expression takes account of the coherent relationship between the admixed components. The coefficient $U_K$ is a function of the angular momenta of all transitions preceding that observed. For the unobserved transition

$$I_0 \xrightarrow{L'} I_1$$

the $U_K$ is given by

$$U_K = \left[ \frac{1}{2} \left( 2I_0+1 \right) \left( 2I_1+1 \right) \right]^\frac{1}{2} (-1)^{I_0-I_1-L'} \cdot W(I_0I_0I_0; \text{KLI})$$

When unobserved transitions with mixed angular momenta $L'$, and $L''$ precede that which is being studied, account
must also be taken of any admixture of the modes of decay. In this case, the cross terms due to interference of the admixed components vanish and one has only to replace $U_K(\mathcal{L}')$ by

$$\frac{[U_K(\mathcal{L}') + \delta^2 U_K(\mathcal{L}'')]}{(1+\delta^2)}.$$ 

If there is a series of unobserved preceding transitions the value of $U_K$ is simply the product of the $U_K$'s for each transition. That the preceding transitions involve beta-decay or gamma-decay is of no significance in the determination of the expressions.

The number of terms in equation (4.1) is limited by

$$K \leq 2I_0, \ 2I_1, \ 2L.$$ 

It has been assumed in the above discussion that the final state of the system is a function only of the initial nuclear orientation and the succeeding radiative decays. If intermediate state reorientation occurs then expression (4.1) must be replaced by

$$W(\theta) = \sum_{K \text{ even}} Q_K^B K^U K^F K^P (\cos\theta)$$  \hspace{1cm} (4.4)

where $Q_K$ describes the attention or enhancement of the anisotropy due to the intermediate state reorientation. However, no significant reorientation will occur if the
lifetime of the intermediate state is small compared to the Larmor precession time of that state.

4.2 The Nuclear Orientation Parameters of $^{103}$Ru in Iron

Shown in figure 4.1 is part of the decay scheme of $^{103}$Ru based on the analysis of Avignone and Fray (1967), Raeside et al. (1969) and Pettersson et al. (1970). The gamma-ray spectrum is dominated by two peaks: a strong peak at 497 KeV and a weaker peak at 610 KeV of only 6.2% the intensity of the 497 KeV peak. For the 497 KeV transition the Fermi/Gamow-Teller mixing ratio of the preceding beta decay has not been determined. For the succeeding gamma radiation, the E2/M1 mixing ratio has been determined (Pettersson et al., 1970) only to the extent that $\delta^2(E2/M1)$ is between .01 and .17. For the 610 KeV emission the preceding beta transition is pure Gamow-Teller. The gamma-ray multipolarity can be M1 or E2, but the mixing ratio is not known.

The nuclear orientation coefficients $F_K$ and $U_K$ for the possible decay modes are given in table 4.1. It should be noted in particular that the cross term giving the mixing of M1 and E2 for the 497 KeV transition is
Figure 4.1 The Decay Scheme of $^{103}$Ru.
TABLE 4.1

$U_K$ and $F_K$ Coefficients for $^{103}$Ru

<table>
<thead>
<tr>
<th>$\gamma$-Transition</th>
<th>Beta Decay ($U_K$)</th>
<th></th>
<th>Gamow-Teller</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fermi U2</td>
<td>U4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>497 KeV</td>
<td>1.00</td>
<td>1.00</td>
<td>0.657</td>
<td>-0.143</td>
</tr>
<tr>
<td>610 KeV</td>
<td>-</td>
<td>-</td>
<td>0.875</td>
<td>0.580</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Gamma Decay ($F_K$)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_1$</td>
<td>$E_2$</td>
<td>$M_1/E_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$F_2$</td>
<td>$F_4$</td>
<td>$F_2$</td>
<td>$F_4$</td>
</tr>
<tr>
<td>497 KeV</td>
<td>0.134</td>
<td>0.325</td>
<td>0.118</td>
<td>0.694</td>
</tr>
<tr>
<td>610 KeV</td>
<td>-0.436</td>
<td>0.249</td>
<td>-0.478</td>
<td>-0.378</td>
</tr>
</tbody>
</table>
large giving a very sensitive measure of this mixing.

Using the Mossbauer technique, Kistner (1969) has determined the hyperfine field of ruthenium in iron to be

$$H_{hf} = 500 \pm 10 \text{ KG}$$

The nuclear magnetic moment of $^{103}\text{Ru}$ is not known. The nucleus has 44 protons and 59 neutrons. There are 9 neutrons above the magic number 50. Using the shell model for neutrons, these 9 neutrons will be distributed between a $2d^{5/2}$ level and a $1g^{7/2}$ level which are closely spaced in energy. Because of the large number of nucleons involved the calculation of the magnetic moment would be complicated. The Schmidt limits for this nucleus ($I = 5/2$) are

$$-1.91 \mu_N < \mu < 1.36 \mu_N$$

4.3 The Experimental Procedures

Preparation of the specimen of $^{103}\text{Ru}$ in iron was straightforward. Some $^{103}\text{RuCl}_3$ in HCl was evaporated to dryness on an iron foil of dimensions 1.0 cm x 0.8 cm x 0.03 cm. The ruthenium replaces some iron which is less electronegative. The foil was heated at about 900°C for 72 hours to diffuse the ruthenium; the surface layers
were then etched off with HCl to remove residual surface activity. The resulting activity of the specimen was 5 to 10 μCi. Several specimens were prepared for the experiments.

The specimen was soldered to one side of the copper heat sink. A $^{60}$Co-Fe thermometer was soldered to the other side. The demagnetization assembly used a cerous magnesium nitrate salt pill with a manganous ammonium guard pill. The lowest temperatures recorded with this assembly were about 9 mK.

Initial experiments indicated only a small anisotropy was present in the $^{103}$Ru 497 and 610 KeV transitions. Because it would be necessary to correct the ruthenium counts very carefully for any anisotropic $^{60}$Co background, a separate $^{60}$Co run was performed in order to determine the $^{60}$Co spectrum in the experimental configuration. Two $^{103}$Ru in iron experiments were performed. In the first $^{103}$Ru experiment the $^{103}$Ru source had an activity of 8 μCi and the $^{60}$Co-Fe thermometer had a $^{60}$Co activity of 5 μCi. To improve the background correction further the second $^{103}$Ru experiment was performed with a $^{103}$Ru activity of 28 μCi and a $^{60}$Co activity of only 0.8 μCi. For this second experiment the $^{60}$Co background in the $^{103}$Ru peak was about 1%. The temperatures obtained in the first experiment were in the region of 9 mK to 13 mK whereas in
the second experiment with the larger $^{103}\text{Ru}$ source the lowest temperature recorded was only 10 mK presumably because of the increased radioactive heating.

The gamma-radiation was measured by two Ge(Li) detectors, placed in the axial and equatorial directions. It was discovered that the equatorial detector was affected ($\sim 1\%$) by the magnetic field of the main magnet. This gave cause for some uncertainty in the equatorial counts measured in the first experiment in which the normalization counts were taken with the main magnet on. The equatorial counts were therefore discarded for that experiment.

4.4 Analysis of the Spectra

The $^{60}\text{Co}$ background, which is scattered radiation, has an anisotropy which has the same temperature dependence as the $^{60}\text{Co}$ peaks but not the same angular dependence. Hence, the background run (no $^{103}\text{Ru}$ specimen) was analysed to fit the background in the window of each of the $^{103}\text{Ru}$ peaks to the anisotropy of the $^{60}\text{Co}$, for each detector. Using this fitted background in the $^{103}\text{Ru}$ runs the peaks could be corrected for the $^{60}\text{Co}$ background.

Another method used to determine the background in the $^{103}\text{Ru}$ peaks assumed that the background was linear in the region of the peak. The background in the peak was
then estimated by measuring the background above and below the peak. The background-corrected counts determined by the linear method were compared to those determined by the fitted method. For the first run the agreement of individual counts was within 0.8% with no systematic variations. For the second run the agreement was within 0.1%. The agreement of the linear method and the fitted method indicates that the background correction is reliable.

In the actual analysis of the spectra the $^{103}$Ru peak intensity was determined by subtracting the background which could be calculated from the $^{60}$Co anisotropies and intensities. The $^{103}$Ru intensity was then corrected for the decay of the source during the experiment (about 2%) and statistical errors were determined.

The final anisotropies are given in table 4.2. Evaluation of the temperature dependence of 497 KeV transition would allow the determination of the magnetic moment of $^{103}$Ru independently of the decay parameters. Hence, the anisotropies have been grouped by temperature. Unfortunately, in the first run the error was too large to determine the temperature dependence accurately enough, whereas in the second run sufficiently low temperatures were not achieved.

The 610 KeV transition was too weak to give significant results in the first run. In the second run
# TABLE 4.2

$^{103}$Ru Anisotropies

### 497 MeV Transition

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature Range (mK)</th>
<th>$1 - W(0)$</th>
<th>$W(\frac{\pi}{2}) - 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9 - 10</td>
<td>0.010 ± 0.0016</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>10 - 13</td>
<td>0.0059 ± 0.0018</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>10 - 12</td>
<td>0.0048 ± 0.0007</td>
<td>0.0025 ± 0.0005</td>
</tr>
</tbody>
</table>

### 610 MeV Transition

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature Range (mK)</th>
<th>$1 - W(0)$</th>
<th>$W(\frac{\pi}{2}) - 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10 - 12</td>
<td>0.004 ± 0.003</td>
<td>-0.001 ± 0.002</td>
</tr>
</tbody>
</table>
the results are sufficient only to conclude that the anisotropy, 1-W(0), is less than ±0.005.

4.5 Analysis of Anisotropies

Because of the small anisotropies observed, the fourth order term in the expression for W(0) can be ignored giving the simplified equation

\[ W(0) = 1 + B_2 U_2 F_2 \]

The fact that for the 497 KeV transition

\[ W(0) < 1.0; \quad W\left(\frac{\pi}{2}\right) > 1.0 \]

clearly indicates that \( F_2 \) is negative for this transition. This means \( \delta \) must be negative and, since it is established that \( \delta^2 (E2/M1) \) is between .01 and .17, we have the result

\[ -.41 < \delta < -.10 \]

Choosing the mixing ratios for the beta and gamma decays which give the largest possible effect yields the maximum value for \( U_2 F_2 \):

\[ U_2 F_2 < .33 \]

Allowing only the smallest value for the observed anisotropy,

\[ 1 - W(0) = 0.004 \]
at 11 mK gives the lower limit of \( B_2 \): 

\[
B_2 > \frac{.004}{.33} = 0.012
\]

and therefore, for a hyperfine field of 500 KG and spin 5/2, the nuclear magnetic moment is given by

\[
\mu_I > 0.15\mu_N
\]

The observation that the effect for the 610 KeV transition was less than ±.005 means

\[
|B_2U_2F_2| < .005
\]

Using the above result, \( B_2 > .012 \), yields

\[
|F_2| < .42
\]

From equation (4.3), the mixing ratio for the 610 KeV transition is therefore limited to

\[
\delta(E2/M1) < 0.0 \quad \text{or} \quad \delta(E2/M1) > 1.1
\]

Since this work was completed measurements on the same system have been made by Krane and co-workers (Krane, 1976) at temperatures as low as 5 mK. A value of \( B_2U_2F_2 = -0.020 \pm 0.001 \) was obtained for the 497 KeV radiation. The temperature dependence of the anisotropy in the temperature range 5 mK - 8 mK was used to determine
the nuclear magnetic moment, the value obtained being

\[ \mu = 0.67 \pm 0.11 \mu_N \]

Our result is consistent with this more accurate value.
CHAPTER V

Nuclear Orientation of $^{59}\text{Fe}$

5.1 Introduction

Nuclear orientation of $^{59}\text{Fe}$ in the paramagnets Ce-Zn nitrate and Nd-Zn nitrate was observed by Tschanz and Sapp (1970). However, this was a difficult system for interpretation largely because only a fraction of the Fe ions were in lattice sites in the crystal structure. Nuclear orientation in iron is a more direct experiment which could clear up some of the uncertainties in their work.

The decay scheme of $^{59}\text{Fe}$ is given in the handbook of Lederer, et al. (1968). The relevant features are given in figure 5.1. There are two beta emissions with unknown Fermi/Gamow-Teller mixing ratios. The two resulting gamma-rays each have predominantly E2 character. The lifetime of the 1.292 MeV level is rather long being 0.59 nsec. A possible reorientation could occur for this state for very large hyperfine interactions where the nuclear precession is not slow compared to the lifetime of the state. The spin of the $^{59}\text{Fe}$ nucleus is $3/2$. The Schmidt limits for the nuclear magnetic moment, $\mu$, for this spin
Figure 5.1  The Decay Scheme of $^{59}$Fe.
are

\[-1.91 \mu_N < \mu < 1.14\]

The nucleus has 26 protons and 33 neutrons. Using the shell model, there are 5 excess neutrons to fill two closely spaced levels, the $2p^{3/2}$ and $1f^{5/2}$ levels. A higher level $2p^{1/2}$ is unlikely to contribute. Assuming that shells with even numbers of neutrons do not contribute to the magnetic moment, only the configurations

\[(2p^{3/2})^1(1f^{5/2})^4, (2p^{3/2})^2(1f^{5/2})^3, (2p^{3/2})^3(1f^{5/2})^2\]

need be considered. The resultant magnetic moment for three particles in one angular momentum state is given by

\[(I/I_0)\]

times the single particle value where $I$ is the spin of the resultant state and $I_0$ is the total spin of each particle in the state (see for example Rose, 1967). The resultant moments of the three states given above are

\[-1.91 \mu_N, 0.82 \mu_N \] and \[-1.91 \mu_N\]

respectively. It can be seen that this simple model gives a large range of values of the magnetic moment.

The hyperfine field of iron in iron metal has been measured by Hanna et al. (1960) to be 333 KG.

The expression for the intensity of the anisotropic gamma-radiation (4.1) includes only terms as high
as the second order since $2I = 3$, so that

$$W(\theta) = 1 + B_2 U_2 F_2 P_2 (\cos \theta).$$

The $F_2$ coefficients for each gamma-ray have the same value of 0.143. For the same Fermi/Gamow-Teller mixing ratio the $U_2$ coefficients would be equal also. For pure Fermi $U_2$ equals 1.00; for pure Gamow-Teller $U_2$ equals 0.20. At saturation the anisotropy, $1-W(0)$, is 0.143 for pure Fermi and 0.029 for pure Gamow-Teller. At 10 mK assuming $\mu = 1.0 \, N$ the anisotropy would be 0.04 for pure Fermi and 0.008 for pure Gamow-Teller.

5.2 Experiments and Analysis

The $^{59}$Fe source was prepared by neutron irradiation of an iron foil. The initial source strength was 20 $\mu$Ci. The dimensions of the source were $1.0 \, \text{cm} \times 0.8 \, \text{cm} \times 0.03 \, \text{cm}$. A source of $^{60}$Co in iron (2 $\mu$Ci strength) was used for thermometry. The sources were soldered to the copper heat sink. A demagnetization pill made of cerous magnesium nitrate was used to achieve low temperatures. A temperature of about 13 mK was achieved after demagnetization with warming to about 27 mK in one hour.
Two Ge(Li) detectors were used to detect the gamma-radiation. One detector was axial, while the other was in the equatorial plane. The spectra peaks were analysed by subtracting a linear background from each peak as discussed in section 4.4. All anisotropies from the temperature range 13 mK - 14 mK were obtained for each peak in the $^{59}$Fe gamma-ray spectrum. The result, using $A_2 = B_2 U_2 F_2$, was

$$A_2 (1.10 \text{ MeV}) = -0.004 \pm 0.003$$
$$A_2 (1.29 \text{ MeV}) = +0.0044 \pm 0.004$$

5.3 Discussion

Both $^{59}$Fe gamma-rays would be expected to have negative values for $A_2$ regardless of the mixing in the beta-decays. Assume that the mixing is pure Gamow-Teller for both emissions so that a minimum effect occurs. In that case the maximum size of the magnetic moment can be determined from the results. The average value of the effect in the experiments is $A_2 = 0.00 \pm 0.003$ for an average temperature of 15 mK. Therefore, the upper limit on $B_2$ is 0.105 giving

$$u < 0.9u_N.$$
Tschanz and Sapp (1970) observed a value of 
\[ A_2 = 0.05 \] at \( T < 10 \text{ mK} \) for \(^{59}\text{Fe}\) in Ce-Zn nitrate and Nd-Zn nitrate. They estimated that 30% of the nuclei were in crystal sites and they assumed the other nuclei saw a zero hyperfine field and would not contribute to the anisotropy. In this case, the anisotropy for the crystal sites would be given by 
\[ A_2 = 0.17. \] They fitted the temperature dependence of the anisotropy to obtain a rough estimate of the nuclear magnetic moment of the \(^{59}\text{Fe}\) ground state. Assuming the temperature dependence of \( A_2 \) arises solely from \( B_2(T) \) of nuclei in crystal sites they obtained 
\[ \mu = 1.1 \pm 0.2\mu_N. \]
Our measurement for \(^{59}\text{Fe-Fe}\) gives \( A_2 < 0.003 \) at 15 mK which yields 
\[ \mu < 0.9\mu_N \] for pure Gamow-Teller beta decay and 
\[ \mu < 0.4\mu_N \] for pure Fermi decay.

The largest anisotropy occurs if all nuclear spins are in the lowest Zeeman level and if the beta decay occurs with complete Fermi mixing. In this case 
\[ A_2 = -0.14. \] This is approximately the size of the effect seen by Tschanz and Sapp. If it is assumed that their result indicates complete Fermi mixing, then by our results the maximum nuclear magnetic moment is only 
\[ \mu = 0.4\mu_N \] which is then in disagreement with their value based on the temperature fit of the data. It seems reasonable to question the temperature fit of the double nitrate data. Possibly the nuclei not in crystal sites contribute appreciably to the
anisotropy. This effect could change the shape of the temperature curve thereby affecting the derived value of the magnetic moment. A difficulty encountered by Tschanz and Sapp was the measurement of the temperature which was determined from the susceptibility of the double nitrate salts themselves. Ce-Zn nitrate was used below 10 mK; Nd-Zn nitrate was used above 10 mK. Any inconsistency in the temperature would seriously have affected the fitting process.

In order to explain their large experimental value of $U_2F_2$, Tschanz and Sapp have determined an enhancement factor $Q_2$ (see equation 4.4) of about 5 to 7 for both $\gamma$-rays. The enhancement is assumed to arise from intermediate state reorientation. Agarwal et al. (1967) noted an attenuation of the $\gamma-\gamma$ correlation for the 1.29 MeV level of $^{59}$Co for a metallic iron source as compared to ferric and ferrous chloride sources. It is of course possible that the ionic environment gives an enhancement not found in the metal.

Since the completion of this work Krane et al. (1976) have measured the anisotropies of gamma-radiation from the decay of $^{59}$Fe in iron at a temperature of $3.5 \pm 0.03$ mK. They determined the nuclear magnetic moment to be $\mu = 0.29 \pm 0.03\mu_N$ which is consistent with our less accurate result.
Appendix

**Gamma-Ray Spectrum Analysis**

The gamma-ray spectra obtained in the experiments were analysed to determine the relative intensity of the gamma-radiation for the transition of interest emitted in the directions of the detectors. The general procedure employed for the spectral analysis can be illustrated by considering a typical spectrum obtained in the MnCl$_2$·4H$_2$O experiments from a NaI detector. This is shown in figure A1. The spectrum has one peak from the $^{\text{54}}$Mn decay at 0.835 MeV and peaks from the $^{\text{60}}$Co decay at 1.17 and 1.33 MeV. The gamma-transition photopeaks are superimposed on a 'background' of counts arising from several contributions. Gamma-rays which have been only partially absorbed in the detector constitute the principal source of the background. The anisotropy of these counts is the same as the photopeak anisotropy for that particular gamma-transition. Another source of the background is radiation which has been scattered into the detector ('degraded radiation'). These counts do not have the same anisotropy as the unscattered counts because they were actually emitted in a different direction. In addition, there are isotropic background contributions from the environment due mainly to degraded $^{\text{40}}$K radiation from the concrete of the building. The total background is
Figure A1. Gamma-ray Spectrum.
the sum of the contributions from all the gamma-ray
transitions present. Hence the background under the $^{54}$Mn
photopeak is different than the anisotropy of the photopeak.

To determine the photopeak count, the background
count under the peak can be estimated and subtracted from
the total peak count. A simple technique was used in the
experiments in which it was assumed that the background under
the peak was linear. Counts in a 'window' centered on the
peak were determined as well as counts chosen symmetrically
above and below the window (as shown in figure Al). The
background in the window was then estimated by interpolating
the counts $B_u$ from above the window (channels $b_3$ to $b_4$) and
the counts $B_2$ from below it (in channels $b_1$ to $b_2$). If the
count in the window (channels $w_1$ to $w_2$) is $C$, then the
background corrected count $P$ is given by

$$P = C - \frac{B_L - B_u}{2(b_2-b_1+1)}(w_2-w_1+1).$$

The background-corrected count $P$ is then the estimated value
of the photopeak intensity. The only source of error in the
estimate of $P$ that affects the value of normalized intensity
$W$ is the background which does not have the same anisotropy
as the photopeak and which is nonlinear. For the $^{54}$Mn peak,
this background is mainly the $^{60}$Co degraded radiation. It
contributes an estimated error, for the $^{54}$Mn decay, of ±2%
of the value of \( P \). For the normalized intensity \( W \) this error is reduced. In the worst case, that is the largest measured anisotropy of 20\%, the error in \( W \) is ±0.4\%, giving an error in the anisotropy of 2\%. This contribution to the total error is less than the error in the angular location of the detector and the statistical error in \( P \). In fact, the other NaI and Ge(Li) detectors used in the experiments had better resolution resulting in smaller background corrections, so that for these detectors the relative error was even less.

Although this method of spectral analysis does not make full use of all the gamma-ray information available in the spectrum, it is very simple and direct, and works satisfactorily for peaks that are well resolved.
REFERENCES


