A dielectric and nuclear magnetic resonance study of lithium hydrazinium sulfate and its deuterated isomorph
by Robert Sanford Parker

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree by
DOCTOR OF PHILOSOPHY in Physics
Montana State University
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Abstract:
Nuclear magnetic resonance measurements have been made on the Li7 spin system-in large single
crystals of LiN2H5SO4. The Li7 relaxation time, T1, has been measured at 14 MHz for temperatures
from 75 °K to 373 °K, and the ND2 deuteron T1 for temperatures from 100°K to 250°K. The activation
energy for the observed relaxation in both the Li7 and ND2 deuteron relaxation for low temperatures is
0.20 ± .02 eV, as previously reported for NH3 and ND3 groups in the respective crystals. The Li7 and
low temperature NDg deuteron relaxation accordingly results from hindered rotation of these groups,
and is shown to be dipolar in all cases. The observed minimum T1's occur at 185°K and are 2.2 sec. in
LiN2D5SO4, 0.52 sec. in LiN2H5SO4 and 4.0 sec. for ND2 deuterons. These data imply that the
LiN2D5SO4 crystal was only 80% deuterated. Also measured were the Li7 quadrupolar coupling
constant eqQ/h and asymmetry η in LiN2D5SO4. As temperature increases from 75°K to 447°K, eqQ/h
decreases from 46.1 to 34.1 kHz and η decreases from 0.69 to 0.46.

Measurements were made of the pyroelectric coefficients in both LiN2H5SO4 and LiN2D5SO4 from
75°X to 150°K. The measured pyroelectric coefficients at 75°K are 11.4 ± 0.3 egs units for
LiN2H5SO4 and 7.6 ± 0.1 egs units for LiN2D5SO4. The pyroelectric polarization is shown to be
irreversible at 75°K confirming that both substances are not ferroelectric.

The observation of "hysteresis" loops has been shown to be consistent with a saturable dielectric. The
model assumed is that of a series of periodically blocked channels along the c-axis. The complex
dielectric constant of such a model is calculated and photographs of predicted behavior are shown. The
inferred mean extrinsic barrier separation is from 6000 å to 15,000 å.
A DIELECTRIC AND NUCLEAR MAGNETIC RESONANCE STUDY OF LITHIUM HYDRAZINUM SULFATE AND ITS DEUTERATED ISOMORPH

by

ROBERT SANFORD PARKER

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Physics

Approved:

Head, Major Department

Chairman, Examining Committee

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana
June, 1971
ACKNOWLEDGEMENTS

The author wishes to thank the National Science Foundation and the National Institute of Health for financial assistance and for providing the equipment and material used in this research. To his advisor, Dr. V. Hugo Schmidt, he owes a great debt for continuous encouragement, understanding, and helpful discussion. To Drs. F. L. Howell and R. R. Knispel he is grateful for helpful discussions, timely preprints, inheritance of equipment, and priceless friendship; even more necessary during the production of a thesis. To Dr. J. E. Drumheller he is grateful for helpful discussions and encouragement given during the terminal stages of the thesis in his advisor's sabbatical absence. He thanks Drs. J. A. Ball and J. B. Hermanson for many helpful suggestions. To Fred Blankenburg he extends thanks for generous assistance with the electronic apparatus. He thanks Cecil Badgley for assistance with the machine work. Dr. Emerson of the Chemistry Department and Drs. J. Hanton and R. Stabb have been most willing to provide assistance and loan of facilities of the Electrical Engineering Department. To Mrs. Barbara Anderson he extends his appreciation for her ability to decipher handwritten chicken scratchings to the typewritten page. Miss Donna Miller he thanks for assistance with typing, English, and constant encouragement.
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ABSTRACT

Nuclear magnetic resonance measurements have been made on the Li\(^{7}\) spin system in large single crystals of LiNgH\(_2\)SO\(_4\). The Li\(^{7}\) relaxation time, \(T_1\), has been measured at 14 MHz for temperatures from 75\(^{\circ}\)K to 373\(^{\circ}\)K, and the ND\(_2\) deuteron \(T_1\) for temperatures from 100\(^{\circ}\)K to 250\(^{\circ}\)K. The activation energy for the observed relaxation in both the Li\(^{7}\) and ND\(_2\) deuteron relaxation for low temperatures is 0.20 ± 0.02 eV, as previously reported for NH\(_3\) and ND\(_3\) groups in the respective crystals. The Li\(^{7}\) and low temperature ND\(_2\) deuteron relaxation accordingly results from hindered rotation of these groups, and is shown to be dipolar in all cases. The observed minimum \(T_1\)'s occur at 185\(^{\circ}\)K and are 2.2 sec. in LiNgD\(_5\)SO\(_4\), 0.52 sec. in LiNgH\(_2\)SO\(_4\) and 4.0 sec. for ND\(_2\) deuterons. These data imply that the LiNgD\(_5\)SO\(_4\) crystal was only 80% deuterated. Also measured were the Li\(^{7}\) quadrupolar coupling constant \(e\eta Q/h\) and asymmetry \(\eta\) in LiNgD\(_5\)SO\(_4\). As temperature increases from 75\(^{\circ}\)K to 447\(^{\circ}\)K, \(e\eta Q/h\) decreases from 46.1 to 34.1 kHz and \(\eta\) decreases from 0.69 to 0.46.

Measurements were made of the pyroelectric coefficients in both LiNgH\(_2\)SO\(_4\) and LiNgD\(_5\)SO\(_4\) from 75\(^{\circ}\)K to 150\(^{\circ}\)K. The measured pyroelectric coefficients at 75\(^{\circ}\)K are 11.4 ± 0.3 egs units for LiNgH\(_2\)SO\(_4\) and 7.6 ± 0.1 egs units for LiNgD\(_5\)SO\(_4\). The pyroelectric polarization is shown to be irreversible at 75\(^{\circ}\)K confirming that both substances are not ferroelectric.

The observation of "hysteresis" loops has been shown to be consistent with a saturable dielectric. The model assumed is that of a series of periodically blocked channels along the c-axis. The complex dielectric constant of such a model is calculated and photographs of predicted behavior are shown. The inferred mean extrinsic barrier separation is from 6000 Å to 15,000 Å.
Chapter I

INTRODUCTION

The compound lithium hydrazinium sulfate (LiN$_2$H$_5$SO$_4$), hereafter denoted LiHzS, was first prepared by Sommer and Weise$^1$ in 1916. The recent interest in both LiHzS and its deuterated isomorph LiN$_2$D$_5$SO$_4$ (LiDzS) was kindled by Pepinsky, et al.,$^2$ in 1958 when they reported their observation of what appeared to be ferroelectric hysteresis loops in LiHzS over the temperature range from -15°C to above 80°C. This placed LiHzS in a fairly small group of solids which are classed as hydrogen-bonded ferroelectrics. Generally, hydrogen-bonded ferroelectrics are studied as a means of gaining insight into the mechanics of hydrogen-bonding and the nature of the ferroelectric phase transition.

A good example of such a study has been the continued effort on KH$_2$PO$_4$ and KD$_2$PO$_4$ begun in about 1955 by Uehling and co-workers at the University of Washington$^3,4,5$ and continued today in several laboratories throughout the world. These studies have provided us with measurements of deuteron migration rates between hydrogen bonds and between the two stable deuteron locations within each hydrogen bond. The intrabond motion is related to the dielectric behavior and the sharpness of the phase transition while the interbond motion is responsible for the electrical conductivity.

"Ferroelectric" LiHzS and LiDzS have been the subjects of several
recent studies.\textsuperscript{6-20} There have been several nuclear magnetic resonance (NMR) studies of the proton line width in LiHzS culminating in the rather extensive studies of the proton and Li\textsuperscript{7} line width and spin-lattice relaxation done by Cuthbert and Petch\textsuperscript{9} and the later studies done by MacClement, Pintar, and Petch\textsuperscript{10} and by Knispel and Petch.\textsuperscript{11} These workers all found evidence of molecular reorientation within the hydrazinium (N\textsubscript{2}H\textsubscript{5}\textsuperscript{+}) ion, but the assignment of the appropriate relaxation parameters could only be made by inference from similar phenomena in other crystals. This uncertainty was lifted by Howell and Schmidt\textsuperscript{12,13} who completed a deuteron magnetic resonance study of LiDzS and concluded that the ND\textsubscript{2} and ND\textsubscript{3} groups rotate with an activation energy of 0.50 eV and 0.20 eV respectively. The high degree of correlation between these hindered rotation data is shown in Table I-1, taken from reference by Knispel and Petch.\textsuperscript{11} In this work the electric field gradient tensor for the Li\textsuperscript{7} nucleus in LiDzS has been measured and the Li\textsuperscript{7} spin-lattice relaxation time has been measured. These NMR studies, along with the present work, are further discussed in Chapters II and IV.

The structure of LiHzS was obtained from a series of x-ray and neutron diffraction studies made from 1963 to 1967.\textsuperscript{13,14,15} These studies revealed a structure consisting of channels formed by interconnected LiO\textsubscript{4} groups and SO\textsubscript{4} groups winding spirally along the c-axis (Fig.I-1a). Within these channels are chains of hydrazinium
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Figure I - 1a  LiH₂S Projected Down the c-Axis.

Figure I - 1b  View of Hydrazine Chain Along c-Axis.
(N₂H₅⁺) ions which are composed of NH₂ and NH₃⁺ groups (Fig. I-1b). The hydrogen locations were found by neutron diffraction studies, while the NMR investigations showed that both the NH₂ and NH₃⁺ groups undergo hindered rotations. In 1969 Ross, at Brookhaven, did a neutron diffraction study on LiDzS revealing a structure quite similar to LiHzS.

Of particular interest have been the studies of the dielectric properties and electrical conductivity. After Pepinsky's original paper, Vanderkooy, Cuthbert, and Petch measured the conductivity of LiHzS and found a high (about the factor of 200) anisotropy in the conductivity and showed that the high conductivity along the c-axis was protonic in nature. Howell, Schmidt, and Knispel found qualitatively similar behavior for the conductivity in LiDzS.

A surprising feature of the conductivity data is that for temperatures above about 100°C the a- and b- axis conductivities rise more rapidly with increasing temperature, approaching the c-axis value at about the temperature at which the crystal decomposes (Fig. I-2).

Of special interest in this study is the strong possibility that LiHzS and/or LiDzS are not ferroelectric but that the so-called hysteresis loops are the result of a non-linear dielectric. That is, the dielectric constant K is in fact not a constant but a limiting function of applied field.
Figure 1 - 2

Best Fit Curves of the Logarithm of Conductivity for LiHzS and LiDzS as a Function of Temperature. (VCP Indicates Results from Ref. 17.) Plot taken from Reference 20.
Lastly, since LiHzS and LiDzS are crystals of space group Pbn2₁, they have no center of symmetry; hence if they are not ferroelectric they should be pyroelectric. The pyroelectric coefficient has been measured to see if the observed pyroelectricity is reversible. This along with the other electric properties of the crystal are discussed in Chapter III.

Chapter IV is reserved for an overall discussion including correlation of the NMR data with the electrical properties which are separately discussed in Chapters II and III, respectively.

Finally, Chapter V contains details and discussions of the experimental apparatus and techniques along with some discussion of the theory associated with these techniques.

One aim of this thesis is to examine the pyroelectric and dielectric characteristics of LiHzS and LiDzS to find if either or both substances are ferroelectric. Further, if they prove to not be ferroelectric, to explain the observation of "hysteresis loops".

The other main objective is to study the Li⁷ static and dynamic environment in hopes of being able to understand more fully the conductivity mechanism along the c-axis and the structural change at high temperatures.
Chapter II

Li$^7$ MAGNETIC RESONANCE

Section 1: Introduction

Nuclear magnetic resonance (NMR) frequently proves to be a useful tool for the study of solids. If the solid of interest contains within its structure a sublattice of suitable nuclear spins and is also reasonably free of paramagnetic electrons, then studies of the locations of the nuclear magnetic resonances and the NMR transition rates frequently provides a sensitive tool for the observation of molecular motions.

There are two NMR experiments which have been conducted in this thesis. The first is basically a static measurement of the electrical and magnetic environment of the nucleus of interest (Li$^7$). The second is the measurement and analysis of the transition rates governing the spin relaxation of the spin system (both Li$^7$ and $^7$D$^2$ were studied). Before examining and discussing the data let's briefly review each type of experiment.

The first case above allows the measurement of the static electric and magnetic environment of the nucleus of interest. Consider a single nucleus of spin I in a large ($\approx 10K$ gauss) magnetic field $H_o$, and also in an electric field described by $\Phi(r,\theta,\phi)$ where the nucleus is located at $r=0$ and interacts with the universe via a Hamiltonian
Figure II - 1

Quadrupolar Shift of Zeeman Levels of a Spin 1 System
\[ H = H_z + H_Q = -\gamma H_0 \cdot \hat{I} + H_Q (\hat{I}, \hat{H}_0, \theta, \phi) \] (II-1)

If the magnetic term is large compared to the quadrupolar term it is convenient to let the spin quantization axis lie along \( \hat{H}_0 \). This means that the \( 2I + 1 \) allowed spin orientations sample \( H_Q \) in a known fashion and can be used to deduce \( H_Q \) (within a sign).

That this is possible can be seen from the following illustration. Consider the case \( I=1 \). Then (see Figure II-1) the addition of the quadrupolar energy to the Zeeman energy lifts the degeneracy of the \( m=1 \) to \( m=0 \) and the \( m=0 \) to \( m=-1 \) transition energies. This means that (for spin \( I=1 \)) one sees not one absorption but two separate absorption lines, and the splitting between these lines is a known function of the orientation of the magnetic field (spin quantization axis) with respect to the electric field gradient (EFG) tensor (crystal axes). The experiment as described in reference 19 is to record this splitting or spectrum vs. some arbitrary rotation angle \( \theta \) about three mutually perpendicular axes (usually the crystallographic axes), from which one can obtain the five independent contributions to the EFG tensor. This tensor is then diagonalized and the results reported are the largest eigenvalue ("coupling constant") and the asymmetry parameter as defined in Eqs. II-2.
This experiment has been done for the $I = \frac{3}{2}$ lithium nucleus in LiDzS and is discussed in Section 2.

The second type of experiment done in this thesis is the study of the spin-lattice relaxation time, $T_1$, as a function of temperature. The relaxation times are a measure of the rate at which the spins change their states in the Zeeman manifold. For example, if one waits sufficiently long the populations of the states will approach a Boltzman equilibrium, that is:

$$\frac{N_n}{N_m} = e^{-\frac{(E_n-E_m)}{kT}}$$

where $N_n$ = the population of the $m_I = i$ Zeeman state, $E_i$ is the energy of that state, and $kT$ is thermal energy at temperature $T$. Now the studies of $T_1$ involve disturbing this equilibrium and examining the manner in which the spin system relaxes back to equilibrium.

For $I = \frac{3}{2}$ the return to equilibrium is always exponential with a single time constant. However, for $I > 1$, depending upon the experimental details, the decay can be non-exponential or exponential with more than one time constant. This point will be discussed as each result is presented.
Experimentally, there are two types of relaxation study methods used. Where the $T_1$'s are long compared to human reaction times, one can manually prepare the spin system with a fixed frequency, fixed amplitude radio-frequency energy source or CW spectrometer. This is done by placing the sample in a fixed frequency, fixed amplitude magnetic field $H_1$, oscillating at frequency $\omega_0$, and sweeping a large Zeeman field (applied at right angles to $H_1$) slowly enough through the resonant field, $H_0 = \gamma \omega_0 > H_1$, to equalize the populations, resulting in no further energy absorption. The field is then swept at a faster rate through $H_0$ at a time $\tau$ following the saturation procedure. The size of the signal observed is proportional to how far the spin system has deviated from equal population and this results in a signal height which is a function of $\tau$ as in Eq. II-4 (see Appendix B).

$$V = V_o \left(1 - e^{-\frac{\tau}{T_1}}\right)$$ (II-4)

The spin-lattice relaxation time $T_1$ is obtained from the slope of a semi-log plot of $(V_o - V)$ vs. $\tau$.

In those cases in which $T_1$ is less than $\approx 60$ seconds, the technique is slightly different. Human reaction times are too long and the switching must be done electronically. It is more convenient, however, to stabilize the Zeeman field at the desired line location and vary the amplitude of the oscillating field, $H_1$. If the sample is subjected to a large oscillating magnetic field pulse ($H_1 \sim 10$ gauss), a resonant
signal which decays rapidly (in ~ 100μs) is observed. This is called the free induction decay. The amplitude of the free induction decay following a second pulse separated from the preparation pulse by a time \( T \) is also described by Eq. 11-4. The details of such relaxation experiments are described in Appendix B.

The relaxation rate \( \frac{1}{T_1} \), can be related to the mean square fluctuation of the magnetic and quadrupolar fields. This relation allows us to use measurements of \( T_1 \) to examine molecular motion effects. Such a study was made on the Li\(^7\) spins in both LiHzS and LiDzS and on the deuterons in the ND\(_2\) groups of the LiDzS crystal. These results are discussed respectively in Sections 4 and 5.

Section 2: Li\(^7\) Quadrupole Spectrum Studies in LiN\(_2\)D\(_5\)SO\(_4\)

The Li\(^7\) NMR quadrupole splitting spectrum was studied from 75°K to 444°K. The observed spectra show no drastic change in the Li\(^7\) environment below \( T=100°C \) but show a fairly rapid change above 100°C.

To first order, the interaction between the quadrupole moment of the Li\(^7\) nucleus and the EFG at the Li\(^7\) site results in the observation of three equally spaced lines. These lines correspond to the \( m = \frac{3}{2} \pm \frac{1}{2} \), the \( m = \frac{1}{2} \rightarrow -\frac{1}{2} \), and the \( m = -\frac{1}{2} \rightarrow -\frac{3}{2} \) transitions. In principle, one can distinguish between the two outer lines (\( \frac{3}{2} \rightarrow \frac{1}{2} \) and \( -\frac{3}{2} \rightarrow -\frac{1}{2} \)) by cooling to a point where the populations of the \( \pm \frac{3}{2} \) levels differ by enough to allow a separation by measuring the signal heights.
Practically, however, the relaxation rate \( \frac{1}{T_1} \), becomes so slow at such temperatures \((T \sim 4^\circ K)\) that severe saturation occurs and no signal is observable. Fortunately this loss of information only results in an ambiguity in the sign of the EFG tensor. A more detailed discussion of the equations and theory for this section is contained in Appendix A.

There are four lithium atoms per unit cell, but the symmetries of the crystal result in only two non-equivalent sites for any one rotation. Consequently the quadrupolar spectra in general contain five lines, the four outer lines being about half as intense as the central \((\frac{1}{2} \rightarrow \frac{1}{2})\) line, due to the degeneracy of that line from each site. The splittings of the 2 pairs of outer lines were then measured as a function of the rotation angle about a known crystal axis and least square fit to a function of the form,

\[
(2\Delta v) = A + B \sin 2\phi + C \cos 2\phi.
\]

(III-5)

The least squares fit coefficients are tabulated in Table II-1. The asymmetry parameter \(\eta\), the coupling constant \(K_{2z}\), and the direction cosines of the principal axes of the field gradient tensor are tabulated in Table II-2. The complete rotation spectra are shown in Figures II-2 through II-6.

Figure II-7 is a plot of the separation of the satellites in the c-axis rotation as a function of temperature. Figure II-7a is taken
TABLE II-1
LEAST SQUARES FIT COEFFICIENTS
FROM EQUATION III - 5

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>Rotation</th>
<th>Coefficients (KH₂)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>X</td>
<td>-14.92 ±8.89</td>
<td></td>
<td>-20.87</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>17.95 0.0</td>
<td></td>
<td>-11.51</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>-3.08 ±25.64</td>
<td></td>
<td>33.87</td>
</tr>
<tr>
<td>300</td>
<td>X</td>
<td>-12.45 ±5.10</td>
<td></td>
<td>-20.04</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>16.13 0.0</td>
<td></td>
<td>-8.41</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>-3.80 ±18.39</td>
<td></td>
<td>29.17</td>
</tr>
<tr>
<td>373</td>
<td>X</td>
<td>-11.50 ±4.28</td>
<td></td>
<td>-19.29</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>15.11 0.0</td>
<td></td>
<td>-7.13</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>-4.09 ±14.74</td>
<td></td>
<td>26.45</td>
</tr>
<tr>
<td>415</td>
<td>X</td>
<td>-10.7 ±2.47</td>
<td></td>
<td>-18.3</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>+14.6 0.0</td>
<td></td>
<td>-6.33</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>-3.96 ±11.97</td>
<td></td>
<td>24.86</td>
</tr>
<tr>
<td>447</td>
<td>X</td>
<td>-9.77 ±1.58</td>
<td></td>
<td>-17.39</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>13.69 0.0</td>
<td></td>
<td>-5.44</td>
</tr>
<tr>
<td></td>
<td>Z</td>
<td>-4.51 ±9.91</td>
<td></td>
<td>23.66</td>
</tr>
</tbody>
</table>
### Table II-2

Li$^7$ COUPLING CONSTANTS, ASYMMETRY PARAMETERS, AND PRINCIPAL AXES IN LiN$_2$D$_5$SO$_4$

<table>
<thead>
<tr>
<th>$T$(°k)</th>
<th>Coupling Constant $K_{zz}$ (KHz)</th>
<th>Asymmetry Parameter $\eta$</th>
<th>Principal Axis Direction Cosines</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\cos\phi_x$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\cos\phi_y$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\cos\phi_z$</td>
</tr>
<tr>
<td>75</td>
<td>46.1</td>
<td>0.686</td>
<td>0.129 ± 0.087</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.286 ± 0.768</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.311 ± 0.198</td>
</tr>
<tr>
<td>300</td>
<td>38.4</td>
<td>0.581</td>
<td>0.081 ± 0.145</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.173 ± 0.518</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.149 ± 0.109</td>
</tr>
<tr>
<td>373</td>
<td>34.8</td>
<td>0.516</td>
<td>0.071 ± 0.144</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.136 ± 0.438</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.108 ± 0.090</td>
</tr>
<tr>
<td>415</td>
<td>32.1</td>
<td>0.498</td>
<td>0.039 ± 0.095</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.075 ± 0.284</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.058 ± 0.052</td>
</tr>
<tr>
<td>447</td>
<td>34.3</td>
<td>0.464</td>
<td>0.034 ± 0.053</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.065 ± 0.158</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.051 ± 0.041</td>
</tr>
</tbody>
</table>
Figure II - 2

Li$^+$ Splitting in Li$_2$D$_5$SO$_4$

$T = 75^\circ$K
Figure II - 3

Li\textsuperscript{7} SPLITTING IN LiN\textsubscript{2}D\textsubscript{5}SO\textsubscript{4} 
T = 300\textdegree K
Figure II - 4

Li\textsuperscript{7} SPLITTING
IN LiN\textsubscript{2}D\textsubscript{5}SO\textsubscript{4}
\( T = 373^\circ K \)
Li Quadrupolar SPLITTING
vs. ANGLE IN LiN$_2$D$_5$SO$_4$

at $T=415^\circ$ K

Figure II - 5
Li Quadrupolar SPLITTING vs. ANGLE IN LiN$_2$D$_5$SO$_4$

at $T = 447^\circ K$

Figure II - 6
from reference 6 and is for LiHzS, while Fig. II-7b is for the same orientation in LiDzS. Also plotted in Fig. II-7b, is the temperature variation of the satellites in the a-rotation ($\Theta_a = 27^\circ$).

The collapsing of the a-axis and c-axis spectra to only three lines occurs at about 180°C for both spectra and the onset of this collapse coincides with the activation energy break in the a- and b-axis conductivities.

The largest difference in the EFG tensor for LiDzS from that for LiHzS is the additional splitting observed in the a-axis rotation. In LiHzS the a- and b-axis rotations contain only 3 lines, indicating that the two sites are identical for these rotations.

Section 3: Li$^7 T_1$ in LiHzS and LiDzS

The Li$^7 T_1$ was studies in both the normal and deuterated crystals. The resulting plots of the transition rates versus inverse temperature showed that the Li$^7$ relaxation in both these crystals at 14 MHz was dominated by interactions with the rotating NH$_3$ and ND$_3$ groups. The plots of $\frac{1}{T_1}$ vs. $\frac{1}{T}$, shown in Figure II-8, show that the relaxation in both crystals in consistent with the standard relaxation theory for a thermally stimulated process.

$$\frac{1}{T_1} = K \frac{\tau_c}{1 + \omega^2 \tau_c} + K \frac{\tau_c}{1 + 4 \omega^2 \tau_c}$$  \hspace{1cm} (II-6)
Figure II - 7
Satellite Separation vs. T for LiHzS and LiDzS
Temperature Dependence of the Li$^7$ Spin Lattice Relaxation Time $T_1$ in LiHzS and LiDzS.
where \( T_c = T_0 \exp \left( \frac{E_a}{hT} \right) \), \( \omega = (2\pi) \cdot (\text{transition frequency}) \), and \( E_a \) is the activation energy for the process causing relaxation.

For slow motions \( \frac{1}{T_1} \) is proportional to \( 1/\omega^2 T_c \); and for fast motions \( \frac{1}{T_1} \) is proportional to \( T_c \). Among other factors, the constants \( K_1 \) and \( K_2 \) contain a term containing spatial parameters, and a term proportional to the square of the amplitude of the fluctuations.

Previous experience has led us to look for the following relaxation mechanisms:

a) quadrupolar relaxation due to rotations of the \( \text{NH}_2 \) and \( \text{NH}_3 \) groups, and tumbling of the \( \text{N}_2\text{H}_5^+ \) ion,

b) quadrupolar relaxation due to translations of the protons (deuterons) via the conductivity mechanism,

c) dipole–dipole relaxation resulting from both of the above.

The \( T_1 \) data as shown in Figure II-8 is quite consistent with options a) and c) above. The activation energies obtained from the slopes of the curves and the preexponential coefficients \( T_0 \), obtained from the location of the peak relaxation are both in close agreement with the appropriate values reported for the \( \text{NH}_3 \) and \( \text{ND}_3 \) hindered rotations in the literature (see Table I-1).

The question now arising is what specific interaction is causing this relaxation? The relaxation in \( \text{LiH}_2\text{S} \) must be dipolar, as hindered rotations of the \( \text{NH}_3 \) group could not be expected to result
in a change in the electrical environment of any neighboring nucleus since the charge of a particle in a scalar quantity. Likewise the rotation of a similar group with deuterons should cause no fluctuations in the lithium EFG.

However, if the crystal is only partially deuterated, then the rotation of such a group could result in a change of the EFG tensor at the lithium site due to small differences in the proton bond from a deuteron bond. Unfortunately, the measurement of the EFG for each orientation of the ND$_2$H group is not possible so the only handle we have on it is via relaxation measurements. Before we accept the quadrupolar relaxation hypothesis as the explanation for the observed relaxation, however, we must check on the magnitude of the dipolar relaxation due to an ND$_3$ group. Also, that due to an ND$_2$H group. The method of such calculations is outlined in Appendix B. The calculation for the dipole relaxation rate results in the formula in Equation II-7.

\[ \frac{1}{T_1} = \frac{2}{5} (\gamma_{Li})^2 (\gamma_p)^2 (I_p)(I_p+1)(1-D)(\gamma_d)^2 (I_d)(I_d+1)D \times \left\{ \text{spatial factor} \times \frac{T_c}{1+\omega} \right\} \]

where $\gamma_{Li}$, $\gamma_p$, $\gamma_d$ are gyromagnetic ratios of Li$^7$, H$^1$ and D$^1$ respectively and $D$ is the fraction of deuteration. $I_p$ and $I_d$ are the spins of the proton and deuteron respectively. The magnitude of the relaxation as a function of $D$ normalized at $D=0$ is shown in Figure II-9.
Figure II - 9

Relative Relaxation vs. Fractional Deuteration D

\[ f(D) = \{1 - D(0.937) \} \]
The spatial factor in equation II-7 has been calculated numerically on the computer. The dipolar relaxation contributions for each rotating \( \text{NH}_3 \) group in the closest unit cell to the given \( \text{Li}^7 \) and for each adjacent unit cell were calculated and added. The resultant spatial factor for the \( \text{Li}^7 \) relaxation is

\[
\sum_{\text{factor}} = 8.92 \times 10^{-3} \, (\AA)^{-6} \quad \text{(II-8)}
\]

where \( \tilde{H}_o = H_o \hat{a} \) and the spacings taken from Reference 13. Using this calculation for \( \frac{1}{T_1} \text{Li} \) due to all adjacent \( \text{NH}_3 \) groups results in a calculated \( T_1 \) at \( \omega_o = (2\pi)(14\text{MHz}) \) of:

\[
\left( T_1 \right)_{\text{Li}} \sim 0.34 \text{ sec.}
\]

The observed relaxation in the "deuterated" crystals then corresponds to \( \sim 80 \) to \( 85\% \) deuteration. \( \left( T_1 \right)_{\text{Li}} \) for \( D=1.0 \) is 8.6 seconds.

There still exists the possibility of quadrupolar relaxation, and a calculation of the expected quadrupolar relaxation is not possible since we don't know the EFG tensor for each of the three \( \text{ND}_2\text{H} \) orientations. An order of magnitude calculation has been made, however, by assuming that the EFG fluctuations causing relaxation were those of a lithium going from a fully deuterated to a protonated crystal. This calculation which is order of magnitude at best results in a relaxation rate about a factor of four smaller than that experimentally observed.
The other piece of evidence supporting the dipolar relaxation is the result of the study of the $T_1$ of the ND$_2$ deuterons at low temperature. This work is discussed in Section 4 of this chapter.

The final point to consider in this discussion on the Li $T_1$ measurements is the experimental technique used and the problems encountered. There exists no orientation where both the non-equivalent Li$^7$ sites overlap and aren't separated. That is, in order to be able to saturate all transitions one needs to remove the splitting of the three (for $I = \frac{3}{2}$) lines. If we wish to simultaneously observe both types of lithium sites, the crystal forces one to an orientation with $H_0$ along one of the crystal axes as can be seen from Figures II-2 to II-6. Consequently, the measurements of $T_1$ were made with $H_0$ along $b$ where the two sites are equivalent, but where there are three separate absorption lines. This necessitated a special approach to the problem. The technique used was to use a saturation procedure which saturated all three separate lines and then to monitor the recovery of one of the outside lines.

In order for this technique to be valid it is necessary for the crystal to supply some conditional transition matrix elements which are not described in the normal rate equations. These matrix elements are of the mutual spin flip type and tend to equalize the spin temperature throughout the sample. The hypothesis that such elements exist was checked at several temperatures and confirmed. These matrix
elements do not effect the spin-lattice relaxation directly, but do serve to maintain a uniform spin temperature within the Zeeman manifold. The techniques for saturation and observation of the nuclear resonances is discussed in detail in Chapter 5.

Section 4: $T_1$ Study of the ND$_2$ Deuterons for $100^\circ K < T < 250^\circ K$.

As an additional check on the character of the Li relaxation rate, $T_1$ was measured for the ND$_2$ deuterons for $T$ from $100^\circ$K to $250^\circ$K. The results, shown in Figure II-10, are consistent with the partially deuterated crystal model discussed in Section 3 and Appendix B.

The theory for this relaxation is further complicated by the presence of the hindered rotation of the ND$_2$ groups themselves. The ND$_2$ groups undergo rotations with an activation energy of 0.50 eV and a correlation time $\tau_c$ given by (see Table I-2):

$$\tau_c = \tau_0 \exp \left\{ \frac{E_a}{kT} \right\} = (2.2 \times 10^{-14}) \exp \left\{ 0.50/kT \right\}. \quad (II-9)$$

This means that even though the ND$_2$ group may be rotating slowly enough to evidence two separate lines, the two deuteron sites may be mixing strongly enough to effect the spin-lattice relaxation. In general when $\tau_c > T_1$, the two ND$_2$ sites relax independently and the dipolar relaxation need be calculated only for the site of interest. However when $\tau_c < T_1$, the two deuteron sites are mixing at a fast enough rate that the appropriate relaxation term is the average over
Figure II - 10

Temperature Dependence of the Deuteron Spin Lattice Relaxation Time $T_1$ in LiD$_2$S.
both sites. This effect goes in the correct direction and has about the right magnitude to account for the asymmetric nature of the observed ND\textsubscript{2} relaxation curve.

The dipole sum program yields the following angular sums for the H(1) and H(2) sites taken from Reference 13 (see Eq. II-7) for b\parallel H\textsubscript{0}:

\[ \sum H(1)\{\text{spatial}\} = 1.32 \times 10^{-2} \langle \mathbf{\alpha} \rangle^{-6} \]

\[ \sum H(2)\{\text{spatial}\} = 3.84 \times 10^{-3} \langle \mathbf{\alpha} \rangle^{-6} \]

The peak relaxation in the ND\textsubscript{2} T\textsubscript{1} curves is T\textsubscript{1} \sim 4 sec. or

\[ \frac{1}{T_{1}} \approx 0.250 \text{ (sec}^{-1} \text{) at } T \approx 170^\circ\text{K. Using the parameters from Eq. II-9 we find that } T_{c} \sim 4 \text{ sec. at } T \approx 180^\circ\text{K.} \]

This means that at the peak of the ND\textsubscript{2} curve we are in the region where \( \tau < T_{1} \) and the relaxation is the average relaxation from both sites. The dipolar relaxation is then the same as that seen in Section 3, Eq. II-7, but with the \( \gamma_{Li} \) replaced by \( \gamma_{d} \) (gyromagnetic ratio of the deuteron). This calculation results in a relaxation rate \( \frac{1}{T_{1}} \) of:

\[ \frac{1}{T_{1}} = 0.471 \text{ sec}^{-1} \]

The measurements of the ND\textsubscript{2} deuteron T\textsubscript{1}'s were complicated by the fact that the spectrum consists of eight lines (at T \sim 200^\circ\text{K}).
Furthermore, there is no simple orientation which allows simultaneous observation of both of the ND₂ deuterons. The chosen orientation, b || H₀, allowed irradiation of one satellite of the ND₂ spectrum where the two ND₂ groups spectra are merged. Unfortunately this also resulted in a decay which had two time constants. But the temperature dependence remains unchanged from that for a single decay.

The data, shown in Figure II-10, shows the peak in $\frac{1}{T_1}$ associated with the ND₃ hindered rotation as also seen in the lithium relaxation. The rest of the data points shown as circles and solid circles are points corresponding to the ND₃ $T_1$'s and the high temperature ND₃ and ND₂ $T_1$'s and are taken from reference 20.
Chapter III

"FERROELECTRIC" PROPERTIES

Section 1: Introduction

Of particular interest in this study of LiHzS and LiDzS has been the great likelihood that these crystals are not in fact ferroelectric. That they might not be ferroelectric has been suggested for several years, in particular by Niizeki and Koizumi \(^{15}\) and by Furuhuta.

Niizeki and Koizumi completed an x-ray study in 1963 in which they noted that polarization reversal for chemically equivalent domains would require considerable rotation of the SO\(_4\) tetrahedra, which are nearly colinear with the c-axis. Their x-ray results showed no such reorientation and this fact along with Furuhata's\(^{21}\) observations of dielectric phenomena led them to suggest a search for some alternative explanation for the apparent hysteresis loops.

This thesis contains several studies which confirm the belief that indeed LiHzS and LiDzS are not ferroelectric. They are discussed in Sections 2, 3, 4 and are respectively a study of the crystal surfaces (for planes \(\perp C\)) for "oppositely polarized" crystals, a study of pyroelectric coefficients, and a study of the c-axis dielectric constant saturation with a demonstration of how dielectric saturation can be an alternative explanation of "hysteresis loops".
Section 2: Surface Effects.

The observation by Niizeki and Koizumi that polarization reversal requires large orientational displacements in the SO₄ tetrahedra lends itself to other experimental tests. The rotation of these SO₄ groups would be expected to make the +c-axis look like the -c-axis. This should be observable if there is any microscopic difference in these two surfaces. In fact, it has been noted while looking at the surface of a, b planes (-c-axis) that etching the surface of such planes results in the observation of striations running parallel to the b-axis, but only on one end of the crystal, the other end remaining clear.

This technique was applied to one crystal each of LiHzS and LiDzS and the two faces perpendicular to C were polished and photographed and then etched and re-photographed. Following this first procedure the crystal was subjected to a high field and the polish, etch, and photograph procedure repeated. The polarization voltage was then re-applied in the opposite direction and the observation steps repeated. In all cases for both substances the striations started on one face and never moved. Copies of these photographs are shown in Figure III-l.

This experiment confirms that there is no gross structural change in LiHzS and LiDzS due to a change in polarization. Since the published coercive field is 320V/cm and the field applied at room temperature, was about 2500V/cm, any polarized domains should have reversed
Figure III - 1
Photographs of Etched Crystal
if they could. Lacking any evidence of their reversal we can infer
that the ferroelectricity is not present at least via this SO\textsubscript{4}\textsuperscript{--} reversal
mechanism.

Section 3: Pyroelectric Study of Li\textsubscript{2}HzS and LiDzS

Since the structures of both Li\textsubscript{2}HzS and LiDzS are not centro-
symmetric it is expected that they will be ferroelectric or at least
pyroelectric. Generally any crystal lacking a center of symmetry
will be pyroelectric but those whose pyroelectric coefficients can be
reversed by polarization reversal are also called ferroelectric. This
means that a reasonable test of whether or not a substance is ferro-
electric or not is to measure the pyroelectric coefficient both before
and after reversing the polarization via application of a large
electric field. This experiment was conducted on both Li\textsubscript{2}HzS and LiDzS
with negative results; that is, the pyroelectric coefficient did not
reverse.

The measurements of the pyroelectric charge were obtained by
measuring the voltage across a capacitor placed in parallel with the
sample. The pyroelectric coefficient is the slope of the voltage
versus temperature curve. This slope has been measured for each run
and is plotted against temperature in Figure III-2. As can be easily
seen from these data there is no evidence of polarization reversal,
in spite of the application of a reversing field of ~3000v/cm for
Figure III - 2(a) - Pyroelectric Coefficients in LiH\textsubscript{3}S

- Runs 1 = Unpolarized
- Runs 2 = + Polarized
- Runs 3 = - Polarized

Figure III - 2(b) - Pyroelectric Coefficients in LiD\textsubscript{3}S
about 1 hour. Unfortunately, the experimental arrangement was quite crude and was not useable at room temperature. The pyroelectric coefficients were measured from 75°K to 200°K, well below the region where the loops are normally observed. However, since there is no experimental evidence of a phase transition from 75°K to 300°K it is reasonable to assume that the crystals are either ferroelectric at both temperatures or not ferroelectric at both temperatures. Lacking any hint of polarization reversal at temperatures of from 75°K to ~200°K it seems fair to assume that the crystals are indeed not ferroelectric.

The pyroelectricity is known from the study discussed in Section 2 and from x-ray results not to be a result of sulphate reorientation. The only other likely cause is partial reversal of the N-H dipoles in the NH₂NH chains, with the reversal probability increasing with increasing temperature.

Quantitative information concerning the exact nature and origin of the observed polarization charge is not available from this or any other studies now in this literature. Such studies, perhaps along the lines of those done by Chynoweth, would be valuable and should be pursued in the future.

Section 4: Dielectric Non-Linearity

We have so far shown that the surface effects and the pyroelectric coefficients are not consistent with the sulfate reorientation scheme
or with the ferroelectric necessity of reversible polarization. Since these two experiments make it unlikely that LiHzS and LiDzS are ferroelectric we must look for an alternative explanation of the "hysteresis loops" reported by Pepinsky, et al.²

An alternative explanation is that perhaps the dielectric is saturable and what is observed is this saturation. If both the real and imaginary components of the dielectric constant were to saturate at high field, then this explanation would account for both the leveling off of the dP/dE curve and the fact that the loop gets thin at high field.

That dielectric saturation can be the problem is seen by looking at Figure III-3a. These are all x–y plots where the horizontal scale is the applied voltage (Re \( V_o e^{i\omega t} \)) and the vertical scale is proportional to the time integral of the sample current. The complex part of the dielectric constant is proportional to the slope of the semi-major axis of the ellipse and the thickness of the loop is a function of \( \tan \left( \frac{\text{Re}(\varepsilon)}{\text{Im}(\varepsilon)} \right) \). A simple derivation of this is available in Schmidt's article on ferroelectricity.²³ If the dielectric is not linear, that is if \( \frac{\partial \varepsilon}{\partial V_o} \neq 0 \), then the extremities of the ellipse will tend to flatten as in Figure III-3b. If the loop thickness (hence dielectric absorption) also decreases the result looks like a hysteresis loop (Fig. III-3c).
\[ V_H = \text{Re} \{ V_o e^{i\omega t} \} \]
\[ V_V = \frac{1}{C} \text{Re} \{ \int I_{\text{xtal}} dt \} \]

\( \varepsilon' \propto \) Slope of Semi-major Axis
\( \varepsilon'' \propto \text{Tan Semi-major Axis} \)
\( \varepsilon' \) Saturating at High Applied Field
\( \varepsilon', \varepsilon'' \) both Saturating at High Applied Field

Figure III - 3
Examples of Saturation Resulting in Hysteresis Loops
Dielectric saturation has been assumed in this thesis and the experimental and theoretical results seem to confirm this hypothesis.

The investigation of the dielectric saturation was made using the Sawyer-Tower circuit (see Chapter V, Section 3). It consisted of photographing the oscilloscope traces of the x-y plot of the following voltages,

\[ V_H = R_e \{ V_o e^{i\omega t} \} \]

\[ V_v = \frac{1}{C} R_e \{ \int_{X T A L} dt \} \]

where \( V_H = \) horizontal voltage, \( V_v = \) vertical voltage, and \( C \gg C_{X T A L} \).

For the "hysteresis" loops \( V_o \) was made as large as possible, reaching 2000 V/cm in some cases. For the dielectric saturation experiments,

\[ V_H = V_o + V_1 e^{i\omega t} \text{ where } V_o \gg V_1 \]

The "hysteresis" loops are shown in Figures III-4, and III-5, and show distinct saturation effects. Due to the high DC conductivity of the crystal (which results in greater hysteresis width) the photographs used were all taken at 0°C.

After these photographs were taken, the same crystal was subjected to large DC biases with a small superimposed AC signal. The resulting photographs (the electronics were AC-coupled thus suppressing the DC offset) show that both the real part of the dielectric constant (a
Figure III - 4
Photographs of High Field Dielectric Saturation
Figure III - 5
Photographs of High Field Dielectric Saturation
function of the ellipse thickness) and the imaginary part of the dielectric constant (proportional to the slope of the ellipsoidal major axis) decrease with applied field. These photographs for the 60Hz experiment are shown in Figure III-6.

In Figures III-7 and III-8 are plotted the variation of the real and imaginary parts of $\varepsilon$ vs. applied field for the four frequencies used. These plots show that saturation indeed occurs.

In order to explain this saturation and the "hysteresis" loops the crystal has been assumed to be broken into conducting chains along the c-axis. These chains are assumed to be completely blocked periodically along the c-axis but the carriers can diffuse within chains with a diffusion constant $D$ and between adjacent parallel chains with a diffusion constant $\gamma$. The barriers are assumed to be extrinsic, probably due to impurity ions not being removed when the crystals were grown. The impurities are further assumed to be located a distance $2q$ apart in a single channel but not correlated between channels.

The current density within any single channel then satisfies the following equations:

\[ J = \mu(\rho_o + \delta)E - D \frac{\partial \delta}{\partial z} \]  \hspace{1cm} (III-3)

\[ \dot{\delta} = \frac{\partial J}{\partial z} - \gamma \delta + K \]  \hspace{1cm} (III-4)
Figure III - 6


\[ f_0 = 60\text{Hz} \quad T = 0 \ ^\circ\text{C} \]

Hor. Scale = 5 V/div, Vert. Scale = 0.2 mV/div
LiHzS
\( f = 60\text{Hz} \)
\( E_{\text{max}} = 1840\text{V/cm} \)
\( T = 273 \text{°K} \)

LiHzS
\( f = 29\text{Hz} \)
\( E_{\text{max}} = 525\text{V/cm} \)
\( T = 273 \text{°K} \)

Figure III - 7
Plots of Real and Imaginary Part of Dielectric Constant vs. Applied Polarizing Field
LiHzS

$E_o = 500\text{Hz}$

$E_{max} = 1300\text{V/cm}$

$T = 273\text{ °K}$

LiHzS

$E_o = 1\text{kHz}$

$E_{max} = 2200\text{V/cm}$

$T = 273\text{ °K}$

**Figure III - 8**

Plots of Real and Imaginary Part of Dielectric Constant vs. Applied Polarizing Field.
where \( E \) is \( V_g/w \), \( w \) is the crystal thickness, \( J \) is the current density, \( \delta \) is the charge density, and \( K = \int_{-q}^{q} \gamma \delta(z) dz \). The vertical voltage is then,

\[
V = \frac{AN}{2qC} \int_{-q}^{q} J(z) dz
\]

(III-5)

where \( A = \) surface area of the sample \((cm^2)\), \( N \) is the density of hydrazinium chains and \( C \) is the value of the observing capacitor.

What we need to find then is \( \bar{J}(t) \) which can then be plugged into these relations, yielding the observed quantity for comparison to experiment.

Equations III-3 and III-4 constitute a set of coupled differential equations for \( \delta \) in \( t \) and \( z \) whose general solution, obtained by trial and error \(^{30}, 31\) is:

\[
\delta = \sum_{i=1}^{\infty} \left\{ C_n \cosh \left[ \gamma - n \omega \omega D \left( z - \frac{\mu D}{q \omega} e^{i\omega} \right) \right] e^{i\omega t} \right. \\
+ \left. S_n \sinh \left[ \right] e^{i\omega t} \right\} + \frac{K}{\gamma}
\]

(III-6)

This solution for \( \delta \) can then be inserted into Eq. III-3 to yield a solution for \( J(z,t) \). The coefficients \( C_n, S_n \) can now be obtained by rearranging \( J(z,t) \) into the form

\[
J(z,t) = \sum_{n=1}^{\infty} J_n^* (z) e^{i\omega t}
\]

(III-7)
and recognizing that the extrinsic barriers at $z = \pm q$ require that 
$J(\pm q, t) = 0$ or $J'_n(\pm q) = 0$ for all $n$. These conditions result 
in a complicated series of relations which can be used to obtain the 
$C_n$'s and $S_n$'s with $C_{j+1}$ depending upon all the $S_j$, $S_1$ and $C_j$, $C_1$ coefficients. The calculation of these coefficients has been completed 
out to $n = 3$ and should be numerically computed out to at least $n = 9$.

Finally, the desired variable which is needed is the average value 
of $J'_n(z)$ over the length of the chain. Due to the fact that the $J'_n(z)$ 
are odd functions of $z$, the only terms remaining in a series for $J(t)$ 
are the terms in odd powers of $e^{i\omega t}$.

The results of this calculation of $V_v(t)$ are:

$$V_v = V_1 e^{i\omega t} + V_3 e^{3i\omega t} \tag{III-8}$$

where

$$V_1 = \frac{\text{ANp}_0 Uq}{c} \{1 - \tanh \frac{b_1}{b_1}\} \tag{III-9}$$

$$V_3 = \frac{\text{ANp}_0 U^3 b_3^2 q}{3c} \left\{\frac{\tanh b_1}{b_1} + \frac{\tanh b_3}{b_3} \left(\frac{1}{2} \frac{b_2 \tanh b_1}{b_1 \tanh b_2}\right)\right\}$$

and

$$b_n = \left[\frac{(\gamma + ni\omega)}{D}\right]^{\frac{1}{2}}, \quad U = -\frac{\mu E_0}{q i\omega} \tag{III-10}$$
Now, if we expand these for small $b_n$, we find that:

\[
\frac{V_3}{V_1} = -\frac{1}{45} \gamma^* + 3i\omega \left( \frac{eE_0 q}{kT} \right)^2
\]

or

\[
V_v = V_1 e^{i\omega t} + V_3 e^{3i\omega t} = V_1 \left\{ e^{i\omega t} - \frac{1}{45} \gamma^* + 3i\omega \left( \frac{eE_0 q}{kT} \right)^2 e^{3i\omega t} \right\}
\]

If we plot $(V_v) \left( \frac{3D\omega C}{A\sigma_0 N_{V_0}^2} \right)$ vs. $V_H = \text{Re}\{V_0 e^{i\omega t}\}$, we get plots which show good likeness to the observed loops. These are shown in Figure III-9 for $\tan^{-1} \frac{\gamma}{\omega} = 30^\circ$, and for $eE_0 q/kT = 1, 2, 3$.

The natural tendency at this point is to continue adding graphs for different combinations of parameters. However, since the calculation has not been continued out to high orders it seems only necessary to say that the above calculations and discussion have shown that "hysteresis" loops can be the result of a non-ferroelectric phenomenon.

The previous calculation shows how the blocked channel model predicts "hysteresis" loops but does not result in an expression for the AC dielectric constant in the presence of a large polarization field. The description of the latter experiment requires a slightly different calculation.

To describe the AC dielectric constant in a large polarization field we start from the same equations as before, but make some further assumptions. First we assume that the loop we observe is "linear"; that is, looks like an ellipse but not a distorted ellipse. Next we let
Figure III - 9
Sample Plots of "Hysteresis" Loops
\( \gamma = 0 \) for simplicity. This prevents DC conductivity but still allows a complex dielectric constant. Finally we assume that \( J, \delta, \) and \( E \) are harmonic and contain only time dependence up to \( e^{i\omega t} \). Thus, starting with equations III-3 and III-4, we assume that:

\[
E = E_0 + E_1 e^{i\omega t}, \quad E_0 >> E_1, \quad (III-12)
\]

\[
\delta = \delta_0(z) + \delta_1(z) e^{i\omega t},
\]

\[
J = J_0(z) + J_1(z) e^{i\omega t}.
\]

This simplifies the differential equation which must be solved and results in an expression for \( J_1 \) which is:

\[
\ddot{J}_1 = \sigma_o E_1 \left\{ 1 - \frac{2S}{\sinh(2S) \sinh 2\sqrt{\alpha}} \left[ \frac{\sinh^2 \alpha^+}{\alpha^+} - \frac{\sinh^2 \alpha^-}{\alpha^-} \right] \right\}
\]

where \( S = eE_0q/2kT, \alpha^\pm = S \pm \sqrt{S^2 + i\Omega}, \Omega = \omega^2/D \) and \( 2q \) is the length of the hydrazinium chains.

Now, since we have \( \ddot{J}_1 \) we have \( \epsilon_1 \) since,

\[
\ddot{J}_1 = (\ddot{J}_{1r} + i\ddot{J}_{1i}) = (\epsilon_0 \omega) (\epsilon_1'' + i\epsilon_1').
\]

Thus the slope of the photographed ellipses is proportional to \( \epsilon_1' \) and hence proportional to \( I_m \{J_1\} \).

Of interest for comparison purposes then is \( J_1(E_0)/J_1(0) \).

Strictly, for this solution, \( J_1(0) \) doesn't exist, but the limit of \( J_1 \) as \( E_0 \to 0 \) does exist and is used instead.
Recalling that $S = eE_o q / 2kT$, expansions valid for $\Omega << 1$, $S << 1$, and $\Omega << 1$, $S >> 1$, obtained after much arithmetic, are:

for $\Omega$, $S << 1$

$$
\varepsilon_1' = \frac{\sigma_0^2 q^2}{3e_o D} \left[ \frac{4}{5} (S^2) \right],
$$

$$
\varepsilon_1'' = \frac{2 \sigma_0}{15} \frac{\omega q^2}{D} \left[ 1 - \frac{65}{42} (S^2) \right];
$$

and for $\Omega << 1$, $S >> 1$,

$$
\varepsilon_1' = \frac{\sigma_0}{4 e_o} \frac{q^2}{D} \left( \frac{eE_0 q}{kT} \right)^{-2},
$$

$$
\varepsilon_1'' = \frac{\sigma_0}{8 e_o} \frac{\omega q^4}{D} \left( \frac{eE_0 q}{kT} \right)^{\frac{1}{4}}.
$$

Figure III-10 is a plot of $\varepsilon_1' \left[ \frac{3e_o D/\sigma_0 q^2}{15 e_o D} \right]$ and $\varepsilon_1'' \left[ (15 e_o D)/(2 \sigma_0 q^2) \right]$ vs. $2S$. The break between the two limits occurring at around $2S = 1$ can also be used to make an estimate of the mean chain length. Noting from Figure III-10 that at $s = 1$, $\varepsilon_1' \approx 0.54 \varepsilon_1'(o)$ and $\varepsilon_1'' \approx 0.35 \varepsilon_1''(o)$; the graphs of Figures III-7 and III-8 yield the estimates shown in Table III-1.
Figure III - 10

Graph of Real and Complex Dielectric Constants VS Field
As is evident from table III-1, the inferred value of $q$ is frequency dependent, the values for low $f_0$ being the more reliable since the calculation gets better for small $\omega$. The fact that the experimental curves for $\varepsilon$ vs. $2S$ are not quantitatively similar to the theoretical curve can be ascribed to setting $\gamma$ to zero and perhaps a distribution of $q$'s and barrier heights. The calculation does, however, show how an isolated chain of carriers can exhibit a saturating dielectric constant.

<table>
<thead>
<tr>
<th>$f_0$</th>
<th>$q_{\text{from } \varepsilon'}$</th>
<th>$q_{\text{from } \varepsilon''}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>29Hz</td>
<td>13,900$\AA$</td>
<td>17,100$\AA$</td>
</tr>
<tr>
<td>60Hz</td>
<td>9,500$\AA$</td>
<td>10,300$\AA$</td>
</tr>
<tr>
<td>500Hz</td>
<td>5,400$\AA$</td>
<td>6,850$\AA$</td>
</tr>
<tr>
<td>1kHz</td>
<td>3,500$\AA$</td>
<td>4,900$\AA$</td>
</tr>
</tbody>
</table>
Chapter IV

DISCUSSION

Section I - Conductivity Mechanisms and Dielectric Saturation

As was mentioned in the introduction both LiHxS and LiDxS show a remarkable characteristic in their conductivities. As stated before, the c-axis conductivity is much larger than the a- and b-axis conductivities. Furthermore, for T below 100°C all three curves exhibit the same activation energy. (See Figure I-2).

The normal conductivity mechanism has always been thought to be proton or deuteron hopping along the hydrazinium channels parallel to the c-axis. This model accounts well for the anisotropic conductivity if one assumes that inter-channel jumping is less likely than intra-channel motion. However, if the activation energies for the inter- and intra-processes are not equal then the slopes of the log $\sigma$ vs. $T$ curves along separate axes should differ.

The observed curves for T<100°C have the same slope or activation energy thus the low temperature conductivity is dominated for the temperatures by one process. One possibility which would account for this phenomenon is that of blocked channels. If the hydrazine channels are periodically blocked so that charge carriers cannot move freely from one end of the crystal to the other, then the activation energy for the c-axis conductivity would appear to be the same as that
for inter-channel hopping (some activation energy as found for a- and b- axes). The break in the a- and b- axis conductivities at T=100°C, in Figure 1-2, might then be explained by some other, as yet not understood channeling opening up in the a- and b- directions.

The evidence presently available indicates that at these high temperatures the crystal decomposes into Li₂SO₄ with the escape of H₂S, N₂ and H₂O gases, with an activation energy of ~1.35 eV. This decomposition is consistent with conductivity data at high T and also with the observation of crystal clouding at high T and the collapsing of NMR spectra discussed in Chapter II.

Finally, the blocked channel model also predicts the observation of "hysteresis" loops via the non-linear dielectric characteristics of finite chains. The calculations, shown in Chapter III, predict hysteresis-like loops and dielectric saturation similar to that observed.

The conductivity measurements give us a good handle on the value for γ, the inter-channel diffusion constant, and Eγ the inter-channel activation energy. However, they give at best only an order of magnitude estimate of the intra-channel diffusion constant D. A measurement of D would be quite helpful in understanding the mechanism of c-axis conductivity and might be obtained from NMR studies. This point is discussed in Section 3.
Section 2: Pyroelectric Behavior

Any crystal which lacks a center of symmetry could be expected to show pyroelectricity. Further, any reversible pyroelectric is called ferroelectric.

Since LiHzS and LiDzS are centro-symmetric a test of the pyroelectric reversibility is a sensitive test of its ferroelectricity.

The aim of the pyroelectric study completed in this thesis was to determine if the spontaneous polarizations of LiHzS and LiDzS are reversible, and to obtain an estimate of the pyroelectric coefficient, for comparison to the pyroelectric coefficients of similar materials.

The graphs of polarization charge as a function of temperature as shown in Figures III-2a and III-2b show no reversal of polarization and do show an increase in \( \frac{dP}{dT} \) as T increases.

The measured values of the pyroelectric coefficient \( \frac{dP}{dT} \), measured at T = 75°K are:

\[
\frac{dP}{dT}_{\text{LiHzS}} = 11.4 \pm 0.3 \text{ CGS UNITS} \\
= 3.40 \times 10^{-5} \text{ coul/}°\text{K m}^2
\]

\[
\frac{dP}{dT}_{\text{LiDzS}} = 7.57 \pm .1 \text{ CGS UNITS} \\
= 2.27 \text{ coul/}°\text{K m}^2
\]

These values are close to the published values of the pyroelectric coefficients for similar materials.
The main important result of this pyroelectric study is the lack of reversibility of the spontaneous polarization. The magnitude of \( \frac{dP}{dT} \) implies that the pyroelectric mechanism is similar to that found in similar materials, but further study of the possible \( \text{NNNNH hydrazine} \) chain ordering is indicated.

The additional evidence against ferroelectricity provided by the surface examination experiment leaves the possibility of a reversible polarization and hence a ferroelectric character as, at best, a very remote possibility.

Section 3: Structural and Motional Changes at High Temperatures

One of the aims of this thesis has been to shed some light on the apparent "phase" change in both LiHzS and LiDzS at high (>100°C) temperatures. To this end the Li EFG tensor measurements were continued to 175°C and the splittings of the a-axis and c-axis rotations were examined up to 200°C.

The high temperature anomaly in the a- and b- axis has already been ascribed to some sort of crystalline phase change. This change results in a collapsing of the Li\(^7\) spectra at high temperature (see Figure II-7) in both the a- and c- axis rotations. The collapse to three lines is complete for the a-axis rotation by 185°C and not quite complete in the c-axis rotation by 200°C. These data are however subject to further considerations.
These EFG measurements and some other preliminary measurements made on the ND₂ deuterons indicate that indeed there is a phase change at high temperature. Preliminary ND₂ linewidth measurements revealed that the ND₂ deuteron lines broaden and disappear above 170°C. This line of attack bears further investigation as a possible means of obtaining the intra-channel diffusion constant, D.

Preliminary data received from Dr. Arend in Zurich indicates that the crystal decomposes at high temperature possibly according to the reaction:

\[ 2\text{LiN}_2\text{H}_5\text{SO}_4 + \text{Li}_2\text{SO}_4 + H_y S^+ + 4\text{H}_2\text{O}^+ + 2\text{N}_2 \]

If this reaction, requiring the exhaust of several vapors, occurs in the interior of the crystal, then the products might be trapped and if the crystal is cooled soon enough, it might return to the LiHzS form. After prolonged high temperature experiments the crystal shows a white powder crust which might be Li₂SO₄. Dr. Arend further measured dm/dt for some crystal chips obtained from this laboratory and found that the decomposition rate increases with T with an activation energy of \(~1.35\) eV.

The last supposition which now seems expedient concerns the high temperature conductivity. Since the conductivity is thought to be dominated by jumping between hydrazine chains, the break in the a- and b-axis conductivities might be associated with the opening up of
long, low-resistance chains perpendicular to the c-axis. If further these chains are well separated, they would not drastically effect the c-axis conductivity and could explain the conductivity anomaly.

Section 4: Li$^7$ Spin Lattice Relaxation Mechanisms

The Li$^7$ spin-lattice relaxation has been shown to be caused primarily by magnetic dipole interaction with the protons or deuterons in the NH$_3$ hindered rotators. This relaxation mechanism is calculated theoretically and the calculations agree with the experimentally observed relaxation.

Of conceivable future interest is the possibility of repeating some of the $T_1$ measurements at other frequencies. These new experiments would perhaps allow one to determine whether the dipolar relaxation is the only effective relaxation mechanism or whether spin diffusion or quadrupolar relaxation might become effective in some frequency and temperature regions.

The dipolar relaxation rate vs. deuteration fraction curve of Figure II-9 suggests an interesting application. If one would like to measure the fractional deuteration of LiDzS or any other substance which has in its structure hindered rotators containing protons or deuterons, he might quite possibly be able to deduce the fractional deuteron concentration via the spin-lattice relaxation time of some other isolated spin species within the sample. Impurities might
even be used as "probes" for the measurement of the deuteration.

Finally, it is of great interest to consider the possibility of using spin-lattice relaxation studies as a means of deducing the intra-channel diffusion constant D. This might be done by examining $^7$Li relaxation for low T at frequencies above 14 MHz, or by examining the ND$_2$ deuteron linewidth at high temperature.
Chapter V
EXPERIMENTAL TECHNIQUES AND APPARATUS

Section I: Sample Preparation

All samples of both LiHzS and LiDzS were grown by slow evaporation from aqueous solutions. The LiHzS crystals, in particular, were prepared by dissolving stoichiometric amounts of reagent grade Li$_2$CO$_3$ and (NH$_2$)$_2$·H$_2$SO$_4$ in distilled, deionized water which was allowed to evaporate resulting in large (~1/2 in$^3$) single crystals. The mixture going according to the reaction:

$$\text{Li}_2\text{CO}_3 + 2(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4 \rightarrow 2\text{LiN}_2\text{H}_5\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2$$

The solutions were mixed slowly to allow for the controlled escape of the CO$_2$. To obtain the deuterated crystals the original LiHzS crystals were redissolved first in 90% D$_2$O, and the crystals (~50% deuterated) obtained from this solution were repeatedly dissolved and recrystallized in 99.8% pure D$_2$O solutions. This resulted in from 80 to 95% completely deuterated crystals.

After the initial H$_2$O stage the solution evaporation took place in a dessicator to minimize water vapor exchange with the air, and to provide a constant evaporation rate. The seeds were placed in small glass flat-bottomed dishes. Because the bottoms of any commercially available dishes are slightly curved, the bottom was covered with a
piece of microscope slide; providing a very flat surface on which the crystal grows. Use of such a surface for the seed to rest on combined with frequent (~twice a week) turning of the seed and filtration of the solution resulted in very clear fault-free crystals of up to 2 cm length 1 cm² cross section in two weeks to a months time.

The NMR samples were oriented by aligning the external faces in a machine vise and epoxying a bakelite rod onto the sample in the desired orientation. The epoxy used was Techkits #E-63 and seems to hold the crystal well from liquid nitrogen temperature to 200°C, the only failures coming from crystal breakage due to differential expansion strains.

Section 2: Domain Reversal Attempts

The crystal was cut and water polished in the a, b-plane. The resulting smooth faces (one along +c- one along -c-axis) were photographed and then were coated with conducting silver paint. The sample (both the LiDzS and LiHzS samples were ~ 2 mm thick) was then subjected to a field several times larger than the published coercive field ( ~320 V/cm)² for 10 minutes. At the end of this time both end faces were cleaned with methonal and etched with H₂O (or D₂O) for 1 minute and then quickly blotted dry. Both faces were then photographed. This process was then repeated with the electric field reversed and
the photographs retaken. The photographs were taken with a Nikormat camera and a microscope adaptor.

Section 3: Dielectric Measurements

The dielectric non-linearity measurements were made using the equipment already available in the laboratory. The sample probe employed is fully described in Figure 28 of Reference 20. It essentially consists of a guarded sample jig housed in a brass can to keep thermal gradients small.

Due to the leakage resistance of the crystal at room temperature and the resulting heating effects, the sample holder was filled with transformer oil and placed in an ice bath. A thermocouple was used to measure the oil temperature close to the crystal sample. The circuit used is shown in Figure V-1 and was used for all measurements. Adjustments were made only in the gain factors of the oscilloscope and the value of C.

The A-C and D-C voltages necessary to the experiment were obtained respectively from a H.P. 200 CD oscillator and a John Fluke Model 405 B power supply. In order to get sufficient A-C voltage to display the "hysteresis" it was necessary to amplify the audio oscillator with a Heathkit Model W-5M amplifier and series-parallel several high quality audio transformers. This arrangement resulted in 2kv p-p available A-C from 29Hz to 1kHz. The low frequency was chosen at a frequency which
Figure V-1 Dielectric Nonlinearity Measurement Circuit

Figure V-2 Pyroelectric Measurement Circuit
seemed to minimize 60Hz line interference.

Section 4: Pyroelectric Measurements

The pyroelectric coefficients were measured by cooling the crystal to LN₂ temperature then warming relatively slowly (~2°/min) and monitoring the voltage across the crystal. It was necessary to parallel the sample with a large (0.1μf) capacitor because of the large pyroelectric coefficient. Thus, the measured quantity was the voltage across the 0.1μf capacitor, from which the pyroelectric charge was obtained. Fig. V-2 is a diagram of the apparatus.

This experiment was repeated several times on one sample each of LiH₂S and LiD₂S. Between runs the crystal was subjected to a large "polarizing" field several times larger than the coercive field. The LiH₂S sample had no guarding but the results seem fairly consistent. The LiD₂S experiment, using guarded sample #12, was run with the guard grounded and the measured potential obtained from the center contact.

The sample was connected to the heat block by painting the newly cleaned heat block with silver paint (Hanovia #16) and placing the crystal firmly on the wet paint. The signal electrode was first soldered to the access wire, then carefully connected onto the sample by silver paint with care to avoid the possibility of strain on the crystal.
Section 5: CW NMR. Equipment and EFG Measurements

The quadruple splittings and long $T_1$ values were obtained using a Robinson spectrometer\textsuperscript{25} modified by Fred Blankenburg for low-level operation. The circuit was run at 14 MHz and was frequency modulated at ~1000 Hz. The static magnetic field, $H_0$, was provided by a Varian 15" electromagnet with a Model V-FR-2703 Fieldial control.

The crystals were aligned and mounted on bakelite rods which could then be inserted into either the Pulse spectrometer or this CW system. Three crystals were used, one each mounted with respectively the $a$-, $b$-, and $c$-axis perpendicular to $H_0$ or parallel to the cylindrical axis of the bakelite rod. The relative orientation of the crystal could be obtained by noting the rotational location of the bakelite mounting rod which was rigidly affixed to the circular spectrometer base plate which in turn was scribed in degrees.

The procedure used to obtain the EFG spectra was to sweep the field through the location of the center line ($m_I = \frac{1}{2} \rightarrow m_I = -\frac{1}{2}$) using a wide enough sweep to pick up the most extremely split lines. Since the outer lines were never split by in excess of 30 gauss the usual sweep was 50 gauss (in 1 minute). When the lines were well separated, the splitting was measured by recording the separation of the zero crossings of the lines (see Figure V-3a). However, when the lines overlapped, it was necessary to use some other techniques.
Figure V-3
Examples of EFG Measurements
If two lines were overlapping by less than the width of the lines, the splittings recorded were the measured distances from the outer peaks minus 1.5 gauss (the approximate linewidth of the Li\(^7\) lines) and the measured distances of the inner peaks plus 1.5 gauss for respectively the outer lines and the inner lines. If the lines were close enough so that they looked to be coincident, the linewidth(\(\delta H_0\)) of the apparent single line located at \(H = H_0\) was measured and the separations were recorded as \(H_0 \pm (\delta H_0 - 1.5)\) gauss. These latter two procedures are pictured in Figures V-3b, c.

The signal (audio) output of the Robinson spectrometer was detected with a P.A.R. HR-8 lock-in amplifier whose output was recorded on a Moseley Model 7000AR x-y recorder. The frequency of the spectrometer was monitored with a HP 5246L electronic counter.

For those experiments not done at room temperature, the Robinson spectrometer was used in conjunction with a temperature controller that deserves description. The hardware portion of this apparatus shown in Figure V-4, was built in the MSU shop and has been successfully used for temperatures from 75\(^\circ\)K to 475\(^\circ\)K. The outer unit consists of a 1 1/8" I.D. stainless steel tube which runs down to the heat chamber. This tube is heli-arc welded to a coolant tank at the upper end and contains a copper temperature oven at the bottom. The upper end of the copper heat tube has a nichrome resistor wound antimagnetically and electrically insulated from ground. The temperature of the copper
Figure V - 4

CW Temperature Controller
can is monitored with a Cu.-Const. thermocouple, the voltage of which is also used as the feedback control voltage in the electronic temperature regulator. The sample tube is lowered down the center of this heater tube and the region between the controller and sample tube is evacuated and back filled with dry nitrogen. The sample temperature then equilibrates with the controller via conduction of the N₂ gas and empirically stays within ±1°K for the useful range of the controller.

The electronic feedback system for the controller, Figure V-5, consists of a potentiometer which compares a reference voltage to the thermocouple EMF, a null detector which amplifies this error, and a controllable power supply which was built in this laboratory but copied after Kepco's design and shown in Figure V-6.

The system achieves equilibrium for small changes in T (≤20°K) in less than ½ hour, although most experiments were not begun until at least 1 hour of stabilization. After the temperature is established it remains within ±0.5°C.

Section 6: T₁ Measurements

The spin-lattice measurements were made by one of two techniques, depending upon the length of T₁. For long T₁'s (≥22 min) the spin system was saturated by repeated slow sweeps through the resonance lines with the Robinson spectrometer. Following this saturation procedure the magnetic field was shifted off the resonances and after a
Figure V - 5

Temperature Control Apparatus
Figure V-6
Voltage Controlled Power Supply
time $\tau$, swept rapidly through the lines. The signal height, plotted as a function of $\tau$, leads one to $T_1$. For the lithium $T_1$'s at low temperatures (liquid $N_2$ for example), $T_1$ was so long as to make this a good technique for giving reliable values of $T_1$ and a single time constant. The decay for Li$^7$ in LiDzS is plotted in Figure V-7. For the ND$_2$ deuterons at LN$_2$ temperature, the result was also a clean looking decay, although the necessary mechanics of the experiment resulted in a decay with two time constants as shown in Figure V-8. The $T_1$'s shown in Chapter 3 for the ND$_2$ deuterons is the temperature variation of the longer decay constant.

For short $T_1$'s ($\leq$30 seconds) it was necessary to use electronic switching means to saturate and observe the decay. This was accomplished via use of a Pulse NMR spectrometer built in this laboratory for this purpose. This spectrometer, basically a copy of the unit described by Clark,$^{26}$ is outlined in Figure V-9.

Temperature control was accomplished by means of directing liquid nitrogen boil-off across the sample. The rate of boil-off was controlled by placing a resistor in the LN$_2$ reservoir and varying the current through the resistor. In order to achieve equilibrium quicker and to facilitate picking particular temperatures, this system utilized the same feedback control system and controllable power supply as was described in Section 4 of this chapter. Achievable temperatures using this system were from 100$^0$K to room temperature, although
Figure V-7
Example of Li⁷ spin decay

\( T = 75 \text{°K} \)
\( T_1 = 4.84 \text{ hr} \)
Figure V-8
Example of ND$_2$ Deuteron Spin Decay
Figure V - 9

Block Diagram of Pulse Spectrometer
due to the size of $T_1$'s measured, it was only used for $100^\circ K \leq T \leq 250^\circ K$.

Although described fully in Knispel's thesis, the pulse head is pictured in Figure V-10 for completeness.

For the $Li^7 T_1$ measurements in both LiH$_2$S and LiD$_2$S it was necessary to saturate all the lines in a system which had three lines spread over about 25 gauss and then to monitor the recovery of only one of the outside lines. In order to accomplish this the saturation was done by a series of short (~20μs) pulses whose Fourier spectrum was wide enough to assure saturation of all lines. The recovery monitoring pulse, occurring at $t=t_\text{r}$ later, was a single ~500μs pulse. This system worked quite well and resulted in good, single time constant recoveries as shown in Figure V-11.

The pulse experiments consisted of subjecting the sample to a large number of short length (~20μs) high-level bursts of magnetic field (at 14 MHz) and then, after a time $t$, applying another, longer pulse (of length ~500μs) and measuring the amplitude of the decaying magnetization following this long pulse. The amplitude of the decay was, in all cases, measured with a gated or boxcar integrator whose output was measured using a J. Fluke Model 801 D. C. differential voltmeter.
Figure V - 10
Pulse NMR Head (From Reference 27)
APPENDIX
APPENDIX A - Quadrupolar splitting

Due to the electric quadrupolar interaction, the normally degenerate transitions between Zeeman levels are split. In fact, the quadrupolar interaction results in modification of the Zeeman levels (labeled by $I_Z = m$) by the amount (to first order):

$$\Delta E = \frac{eQ}{2I(2I-1)} \left[ 3m^2 - I(I+1) \right] \left( \frac{1}{2} \right) (\phi_{zz})$$

where $e$ is the electron charge, $Q$ is the nuclear quadrupole moment, and $\phi_{zz}$ is the second derivative of the electric potential at the nuclear site with respect to $z$, $z\frac{\partial^2 \phi}{\partial z^2}$.

If the crystal is rotated, then the value of $\phi_{zz}$ obtained can be related to some fixed field gradient tensor by the usual rotation operations $R^{-1} H_0 R^*$. It is easily shown that the EFG tensor can be put into the form of equation A-2 by using just such a rotation.

$$\phi_{ij} = \begin{pmatrix}
-eq (1-\eta)/2 & 0 & 0 \\
0 & -eq(1+\eta)/2 & 0 \\
0 & 0 & eq
\end{pmatrix} \quad (A-2)$$

The quantities $\eta$, $eq$, and three direction cosines between the crystal axes and this diagonal tensors' axes provide all the five independent quantities necessary to specify a symmetric, traceless tensor.

The orientational dependence of the splittings of Eq. A-1 are
seen to be dependent upon \( \sin 2\theta \), where \( \theta \) is the rotation angle about an axis which is perpendicular to \( H_0 \) (or \( z \)). This is not surprising, since the quadrupole interaction corresponds to \( L=2 \) in the expansion of \( \Phi(r, \Omega) \). The expected dependence of \( (2\Delta \nu) \), then, as a function of this rotation angle \( \Theta \) is:

\[
(2\Delta \nu) = A + B \cos 2\Theta + C \sin 2\Theta.
\]

This form is identical with that of Volkoff, Petch and Smellie and results in three sets of constants \( A_x, A_y, A_z, B_x, B_y, B_z, C_x, C_y, C_z \) where \( x, y, z \) are the three axes about which rotations are made. These nine measured constants yield the five independent quantities which compose the EFG tensor and permit the calculation of \( \eta, eq \), and the principal axes of the tensor.
APPENDIX B - On $T_1$ Calculations and Measurement Schemes

The calculation of the spin-lattice relaxation time $T_1$ is tedious but straightforward. Most experiments examining the re-establishment of spin system equilibrium are studies of the temperature dependence of the respective transition probabilities coupled with an attempt to infer what interaction or motion might be responsible for the relaxation.

There are mainly two types of calculations which it is necessary to understand. First, when given the transition probabilities $P_{mn}$ for transitions from state $m$ to state $n$, one should be able to calculate the relaxation rates for the spin systems. Second, given a reasonable spin relaxation mechanism, one should be able to derive the $P_{mn}$'s.

The first problem requires the solution of a set of coupled first order differential equations for the spin populations. We are interested in the populations of each of the members of the Zeeman manifold. Let $N_i$ be the population of the $i^{th}$ member of the Zeeman manifold, and $P_{mn}$ the transition probability to go from state $m$ to state $n$, then the populations can be written for spin $\frac{3}{2}$ as in equations B-1.

$$\dot{N}_\alpha = -N_\alpha \left( \sum_{\gamma} P_{\gamma \alpha} \right) + \sum_{\beta \neq \alpha} N_\beta P_{\beta \alpha}$$

(B-1)
where $\alpha, \beta, \gamma$ take on (for a spin $3/2$ system) the values $\pm 3/2, \pm 1/2$.

Now there are some readily available simplifications. First, $P_{a\beta}/P_{a\alpha} = \exp \left[ (E_a - E_\beta)/kT \right]$ is required by Boltzmann's statistics; secondly, at least for the processes of dominant interest in this thesis, $P_{1-1}/P_{2-2} = 0$; and finally, the variable of interest is not $N_\alpha$ but $N_\alpha - N_\alpha(\infty) = n_\alpha$. If we thus change variables and drop terms in $P_{1-1}/P_{2-2}, R_{1-1}/P_{2-2}$, we get, for $\eta_{1/2}^1 = n_{1/2} - n_{-1/2}$ and $\eta_{2}^3 = n_{3/2} - n_{-3/2}$, two equations:

\[
\eta_{1/2}^1 = -\eta_{3/2}^1 (P_1 P_2 + 2n_0) + \eta_3 (P_1 - P_2)
\]

\[
\eta_{2}^3 = -\eta_{3/2}^3 (P_1 + P_2) + \eta_{1/2}^1 (P_1 - P_2) + \eta \Delta (P_2 + \frac{1}{2}P_1)
\]  \hspace{1cm} (B-2)

where $P_1 \equiv P_{1-3/2} P_{3/2} + 1/2, P_2 = P_{3/2} - 1 = P_{1-3/2} P_{3/2} - 1 = 0$.

and $P_{1}^{3/2} = P_1 (1 + \Delta), P_{-1}^{3/2} = P_2 (1 + 2\Delta), \Delta = \hbar \omega/kT$.

The important point to note about these equations is that the solution for $\eta_{1/2}^1$ yields an exponential decay, but has two time constants.

\[
\eta_{1/2}^1 = \eta_{1/2}^1 (0) + Ae^{-2P_1 t} + Be^{-2P_1 t}
\]  \hspace{1cm} (B-3)

Thus an experiment examining $\eta_{1/2}^1$ on the stationary line at the center of the spectrum might not see a single decay constant. For $P_2/P_1 \neq 1$ this could result in a complete determination of both $P_2$
and $P_1$ but nature is seldom that cooperative.

Equation B-3 is, of course, only one of the four "eigenvectors" of equations B-1. For irradiation of only the central line B-3 is the correct solution. However, there are two other saturation schemes of interest. First, for irradiation of both satellite lines the relaxation looks like:

$$n^1_2 = S(t) = A + B(e^{-2P_1t} + e^{-2(P_1 + P_2)t})$$  \hspace{1cm} (B-4)

And for the simultaneous irradiation of all three lines, the appropriate relaxation equation is:

$$n^1_2 = S(t) = A + B(e^{2(P_1 + 4P_2)t})$$  \hspace{1cm} (B-5)

This last relaxation mode was chosen for the $^{7}\text{Li}$ studies done in this thesis. This mode (Eq. B-5) decays with a single exponential and can be monitored via any one of the three lines. Interestingly enough, to have all the lines decay back to equilibrium with this same time constant requires an additional transition probability, one which cannot be included in $P_1$ or $P_2$. It is a conditional probability, but is experimentally justified by the observed decays.

A similar calculation was made for the $\text{ND}_2$ deuteron study. This was a set of three coupled equations and resulted in a non-exponential decay law; that is, a decay with two time constants. This doesn't affect the results of the study as the form of the decay wasn't important, only its temperature dependence.
The second problem we must address ourselves to is the calculation of $P_1$ and $P_2$. In our case these transition probabilities are due to fluctuations in the local fields and can be estimated by using suitable field parameters.

Relaxation processes in magnetic resonance are caused by fluctuations in magnetic and electric fields. The fluctuations always have a Fourier component which is located at the resonance frequency. It is this component which results in relaxation. A stationary material, having no internal fluctuations does not relax. The usual motions considered are stationary random fluctuations of the magnetic field due to dipole fields of particles in the material and stationary random fluctuations of the EFG tensor due to motions in the crystal (in this study, rotation of the ND$_3$ groups).

The calculation for the transition probability from the state $k$ to the state $m$ is standard and will not be covered in detail here.\textsuperscript{29} It basically consists of a time dependent perturbation calculation with a matrix element which is randomly varying in time. This results in a term, which is dependent upon a factor of the form

$$\langle H_{\text{Pert.}}(t) H_{\text{Pert.}}(t + \tau) \rangle.$$  

The final transition probability, which is dependent upon the transition frequency $\omega$, is proportional to the Fourier transform of this term. Now, this term in its present form is a function of both $t$, the absolute time of the experiment and $\tau$, the time difference.
One would expect that the results for the transition probability should be the same today as tomorrow, or yesterday, hence we make the assumption that the perturbation is stationary random, or not dependent upon \( t \) but only \( t \), so:

\[
< \mathbf{H}_p(t) \mathbf{H}_p(t + \tau) > = < \mathbf{H}_p(0) \mathbf{H}_p(\tau) > = < \mathbf{H}_p(0) \cdot \mathbf{H}_p(\tau) > \frac{e^{-\frac{t}{\tau_c}}}{\tau_c}
\]

This assumption results in a usable form for the transition probability \( P_{mk} \):

\[
P_{mk}(\omega) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} G_{mk}(\tau) e^{-i(m-k)\tau} d\tau
\]

where \( (E_m - E_k)/\hbar \), \( G_{mk}(\tau) = <m|\mathbf{H}_p(0)|k><k|\mathbf{H}_p(\tau)|m> \),

the bar denoting an ensemble average over all values of \(<m|\mathbf{H}_p|k>\).

What remains in our calculation is to calculate \( G_{mk}(\tau) \) for the cases of interest in LiDzS and LiHzS.

This has been done for both the Li\(^7\) nucleus and the ND\(_2\) deuterons. The calculation for the deuteron relaxation is similar enough to the other calculations that it will not be shown.

We need to calculate the ensemble average for

\(<m|\mathbf{H}_p(0)|k><k|\mathbf{H}_p(\tau)|m>\). The field variable of interest for the dipolar relaxation of the Li\(^7\) is the magnetic field at the lithium site, more specifically the x- and y- components. The z- component fluctuations result in greater linewidth but do not affect \( T_1 \).
Now, \( \overline{H_d^2(\tau)} = \sum_{i,j=1}^{N} \vec{H}_{d_i}(\tau) \cdot \vec{H}_{d_j}(\tau) P\left\{ j(\tau) | i(0) \right\} \) \hspace{1cm} (B-8)

where \( \vec{H}_{d_i} \) is the magnetic field at the lithium for the ND\(_3\) group in state \( i \), and \( P\left\{ j(\tau) | i(0) \right\} \) is the probability that at \( t=\tau \) the system has gone from state \( i \) to \( j \). The summation is over all the states of the system which is \( N=3 \) in this case.

Thus, in this case, if we label the states 1, 2, 3, the ensemble average is:

\[
\overline{H_d^2(\tau)} = \frac{1}{3} \left\{ \vec{H}_1 \cdot P_{11}(\tau) + \vec{H}_2 \cdot P_{12}(\tau) + \vec{H}_3 \cdot P_{13}(\tau) \right\} + \frac{1}{3} \left\{ \vec{H}_1 \cdot P_{22}(\tau) + \vec{H}_2 \cdot P_{23}(\tau) \right\} + \frac{1}{3} \left\{ \vec{H}_1 \cdot P_{33}(\tau) \right\} \hspace{1cm} (B-9)
\]

where \( \vec{H}_i = \left( H_{x_i}, H_{y_i}, 0 \right) \), and the magnetic field of interest is the dipolar field, which is the sum of the dipolar fields of the spins located at the corners of the NH\(_3\) group. This is:

\[
\vec{H}_d = \sum_{i=1}^{3} \frac{\gamma_n^2 \vec{I}_n}{r_i^3} \left\{ \frac{\vec{I}_n \cdot 3(\vec{I}_n \cdot \vec{r}_i) \vec{r}_i}{r_i^2} \right\} \hspace{1cm} (B-10)
\]

where \( \gamma_n \), \( \vec{I}_n \) are respectively the gyromagnetic ratio of the proton or deuteron and the spin state of the same and \( \vec{r}_i \) is the radius vector from the proton or deuteron to the ND\(_2\) deuteron or lithium site.

When the appropriate probabilities are inserted for \( P_{\text{eq}}(\tau) \), and
the terms which contain no \( \tau \)-dependence (thus Fourier analysis to constants) are dropped, we get:

\[
H_d^2(\tau) = \frac{1}{9} \left\{ (A_{12} H_d)^2 + (A_{13} H_d)^2 + (A_{23} H_d)^2 \right\} e^{-\frac{\tau}{\tau_c}} \quad (B-11)
\]

The \( x \)- and \( y \)-components are computed separately, with the result:

\[
\frac{1}{T_1} = \frac{1}{4} p_1 = \frac{1}{4} (\gamma L_i)^2 \left( \frac{H_x + H_y}{1 + \omega^2 \tau_c^2} \right) \quad (B-12)
\]

\[
= \frac{1}{4} (\gamma L_i)^2 (\mu_p)^2 \sum_{i=1}^{3} \sin^2 (2\theta_i) \sum_{j=1}^{2} \sum_{k=j+1}^{3} \frac{\sin(2\Theta_j)\sin(2\Theta_k)\cos(\Phi_j-\Phi_k)}{(r_j r_k)} \quad (B-13)
\]

\[
= K \frac{\tau_c}{1 + \omega^2 \tau_c^2}.
\]

This result, pertaining for \( H_0 \) along \( z \); \( \Phi_i \) being the angle between \( \mathbf{r}_j \) and \( \mathbf{k} \), and \( \Phi_j \) the angle made by \( \mathbf{r}_j \) in the \( x \), \( y \) plane.

This result must be further corrected for the statistical problem of a partially deuterated crystal. That is, some of the neighboring \( \text{NH}_3 \) groups may be \( \text{NH}_n \text{D}_{3-n} \) groups and thus result in slower relaxation for \( \frac{1}{T_1} \) as a function of fractional deuteration, \( D \). This gives a result which is identical with Eq. B-12 where:

\[
(\mu_p)^2 + \omega^2 \left[ (\gamma_p)^2 (I_p)(I_p + 1)(1 - D) + (\gamma_d)^2 I_d(I_d + 1) D \right] \quad (B-13)
\]
When evaluated for a NH₃ group located at the closest NH₃ site to a Li⁷ nucleus (locations from P and B), with H₀ parallel to the b-axis, this relation results in a minimum time constant of $T_1 \text{ (min)} = 0.813$ seconds.

The final calculation to be considered is that of the quadrupolar relaxation. This calculation proceeds as above except that due to the lack of information about the quadrupolar fluctuations actually occurring in the crystal an order of magnitude calculation was all that was possible. The fluctuations were assumed to be between two states, in particular the EFG tensor of the fully protonated crystal. The mean square fluctuation then is:

$$H_q^2(\tau) = \frac{1}{4} \left\{ \left[ H_q(D = .1) - H_q(D = 0) \right] ^2 \right\} e^{\frac{-\tau}{T_c}}$$

This results in a peak relaxation rate which is:

$$\left( \frac{1}{T_1} \right)_{\text{Li}} = 0.212 \text{ sec}^{-1}$$

or

$$T_1 = 4.7 \text{ sec}$$

Details of such quadrupolar calculations are found in Appendix B of Howell's thesis.²⁰
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