Abstract:
The nuclear magnetic resonance spectrum of deuterons in LiN₂D₅SO₄ has been studied in detail between 78 and 458°C. The spectrum at 78°C is related to the deuterons of a static N₂D₅⁺ ion. The electric quadrupole coupling constants, the asymmetry parameters, and the orientations of electric field gradient (efg) tensors relative to the crystal axes were obtained at 78, 193, 298, 338, 368 and 438°C. Above 110°C the lines due to the deuterons of the ND₃ group broaden and merge to a single pair of lines which is still evident at 195°C. The lines corresponding to the deuterons of the ND₂ group merge to a single pair between 0°C and 50°C. These line mergers are related to the motion of the ND₃ and ND₂ groups and estimates of the activation energy and jump times of these motions are made. Because of the symmetry of the crystal the absence of line doubling indicates that ferroelectric domain reversal may be due to reflection of the structure through the ab plane.

Measurements of the electrical conductivity and the ac dielectric constant were made on both deuterated and undeuterated samples. The c axis ac dielectric constant was found to be quite large. Estimates of the activation energy and correlation time for the dielectric relaxation were made.

The spin-lattice relaxation times for the merged ND₃ and ND₂ lines were measured over the temperature range from 155°C to 422°C. The results are found to be in good agreement with the assumption that the relaxation is due to fluctuations in the electric quadrupole coupling energy due to ND₃ and ND₂ hindered rotations. In addition, evidence is found to indicate that jumping between ND₂ and ND₃ groups becomes important at temperatures above 75°C. None of the measurements discussed indicate that the crystal undergoes a ferroelectric transition below 200°C.
HYDROGEN BONDING IN LITHIUM HYDRAZINIUM SULFATE

by

FRANCIS LUTHER HOWELL

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Physics

Approved:

[Signatures]

Acting Head, Major Department

[Signatures]

Chairman, Examining Committee

[Signatures]

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

December, 1969
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CHAPTER I INTRODUCTION

An explanation of the ferroelectric behavior of certain hydrogen bonded crystals* derives from understanding the environment and motion within the crystal of the protons forming the hydrogen bonds. X-ray and neutron diffraction studies are commonly used to locate the positions of atoms in the unit cell of the crystal, and may be used to obtain information on the motion of the atoms. Conductivity and dielectric constant measurements also yield information about the motion of the constituents of the crystal.

However, the usefulness of neutron studies to obtain information on motion is limited in the following respect. Since exchange between sites, such as hindered rotation of a group, probably takes place in such a fashion that the time spent "jumping" between sites is a very small part of the total time, the neutron diffraction results will reflect the stationary location of the group. Because of this, neutron diffraction studies give good indication of vibrational or torsional motions, for which time spent out of the equilibrium site is large, but little information

*Discussion of hydrogen bonded ferroelectrics may be found in reference 1. For a detailed discussion of KH$_2$PO$_4$, a representative of this class which has been studied in detail, see references 2, 3, 4, 5, 6, and 7.
about motions such as are of primary interest in this work.

Conductivity studies of hydrogen bonded crystals are difficult. The conductivities commonly encountered are small, \( \sim 10^{-8} \Omega \text{cm} \) or less, and impurities and crystal defects can introduce relatively large errors. At best, measurements of conductivity and dielectric constant deal with bulk properties of the crystal, making it difficult to distinguish the various atomic effects unambiguously.

An experiment which has proven particularly useful in obtaining information about the environment and motion of nuclei is the observation of the nuclear magnetic resonance (NMR) spectrum.*

The nucleus of primary interest is the proton. The NMR spectrum of the proton in solids is generally a single wide line, and proton wide-line NMR studies are limited to measurement of line width and of the spin-lattice relaxation time. From such studies much can be inferred about motion of the protons and their relative location in the crystal. However, no measure of the local electrical environment is possible with the proton since it has no electric moments. Because of their approximate chemical equivalence it is possible to substitute deuterons for

*Discussion of this type of experiment is included in references 8 and 9.
protons. This can be done by crystallizing from a heavy water solution in the case of most water soluble compounds. The deuteron has an electric quadrupole moment and interacts with the electric field gradient (efg) at its location. This interaction modifies its NMR spectrum in such a fashion that the determination of the efg tensor at the deuteron site is made possible.

Lithium hydrazinium sulfate (LiHzS) is a ferroelectric crystal, and neutron diffraction studies of the structure have established that the protons of the hydrazine group are all involved in hydrogen bonds. Nuclear magnetic resonance studies of the protons and Li nuclei in LiHzS have been carried out. Based on these studies, jumping of the protons between bond sites and other motions have been hypothesized.

Although the studies mentioned above answer many questions about the structure and indicate that the protons undergo certain motions, several important questions remain unanswered. Specifically, what are the motions of the protons? Is there a ferroelectric transition below the decomposition temperature of the crystal? What, if any, structural changes occur in the crystal as it is heated? Is there any change in the ordering of the protons when the crystal changes polarization? This work deals with the attempt to answer these questions by a study of the nuclear
magnetic resonance spectrum of deuterons in the deuterated crystal, LiN$_2$D$_5$SO$_4$, and by measurements of the electrical conductivity and ac dielectric constant of the normal and deuterated crystals.

The spectrum of the deuterons was studied below the temperature at which jumping among sites becomes important, and the results are discussed in Chapter II. The NMR spectrum at higher temperature reflects inter-site exchange and the third chapter is devoted to the measurements which reveal this motion. A complete study of the NMR spectrum of the deuterons was carried out to above 150°C. In addition, the deuteron line width was measured as a function of temperature through the critical temperature regions. On the basis of these measurements a calculation of the exchange probability for the motion causing the line width change was done. It was hoped that the electric field gradient measured at elevated temperatures would reflect the structural change suggested by Cuthbert and Petch(12) as a result of their observation of a change in the Li$^7$ NMR spectrum with temperature.

The dielectric behavior was studied because the nature of the dielectric anomaly at a phase transition indicates what type of ferroelectric transition occurs.

Finally the spin-lattice relaxation time was measured
for deuterons of the groups which undergo motion. Using
the efg data discussed in Chapter III, the relaxation
mechanism was related to the fluctuations in the efg due
to exchange between sites. The activation energies for
the motions obtained by the different measurements were
compared.

Relatively few studies have been carried out to deter­
mine the values of the efg tensors at the sites of deuterons
in N-D...N or N-D...O bonds. Because of the numerous
analogies to these bonds found in compounds of biological
significance, it would seem that simply the accumulation of
information about the efg tensors and the activation
energies for motion between bonds of this type is worth
while. Summarized in a table in Chapter II is pertinent
information on some of the nitrogen compounds which have
been studied.
CHAPTER II
DEUTERON ELECTRIC FIELD GRADIENT TENSORS AT 77°K

STRUCTURE

The structure of lithium hydrazinium sulfate (LiN$_2$H$_5$SO$_4$) has been studied by means of x-ray (14, 15, 16) and neutron (11) diffraction. Table I compares the coordinates of the constituents of LiH$_2$S found by these experiments.

LiH$_2$S is orthorhombic of space group Pbn2$_1$ (15) with four molecular units per unit cell. Padmanabhan and Balasubramanian (11) (hereafter denoted by PB) report cell dimensions $a=9.93$, $b=8.969$, and $c=5.178$ Å. Brown (15) has found for the cell dimensions $a=8.99$, $b=9.94$, and $c=5.18$ Å.*

The lithium and sulfur atoms are located at the centers of tetrahedra of oxygen atoms. As is indicated in Fig. 1, these tetrahedra have common apices and form a lattice-work with channels running parallel to the $c$ axis. These channels contain the hydrazinium ions which are hydrogen bonded to atoms in the surrounding lattice and to nitrogen atoms adjacent in the $c$ direction. The

*The exchange in the assignment of the $a$ and $b$ crystal axes by PB will not be followed in this thesis, rather the assignment made by Brown will be observed.
### TABLE I

Atomic Parameters Obtained by X-ray and Neutron Studies

Standard Deviation Is That Quoted by P & B for Their Data

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<td>Balasubramanian</td>
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Fig. 1  A View of LiH2S Projected Down the c Axis. (After Brown(15))

Fig. 2  Two Alternate Arrangements Possible for N-H...N-H... Chain if the Hydrogen Bonds Are Ordered. (After Brown(15))
Fig. 3. Sketch Showing the General Arrangement of the ND$_3$ and ND$_2$ Groups and the Bonding Between Hydrazine Groups.
proton in a hydrogen bond is found at a position between the two atoms with which it forms the bond. In general the proton is nearer to one of the bonded atoms than the other. The bonded atom which is closest to the proton is denoted the donor, and the further bonded atom is called the acceptor. In LiHzS, the donor to proton distances are about 1 Å, and the acceptor to proton distances are roughly 2 Å. The nitrogen is the donor in each N-H...O bond. The nitrogen at the NH₃ end of the N₂H₅ group takes part in three N-H...O bonds. The nitrogen at the NH₂ end is bonded to one oxygen and two other nitrogens. These latter bonds form N-H...N-H... chains along the c direction of the crystal. Following the notation of PB, the proton sites in these bonds are referred to as site 2 whereas the other proton site at the NH₂ end of the N₂H₅ group is in a N-H...O bond and is denoted as site 1. The labeling of sites 3, 4 and 5 is indicated in Fig. 1. From their neutron diffraction study, PB have concluded that most or all of the site 2 protons are ordered in the arrangement pictured in Fig. 2a as opposed to the arrangement in Fig. 2b. They further conclude that no hindered rotation of NH₃ or NH₂ groups takes place at room temperature.

NMR SPECTRUM.

The NMR spectrum of deuterons in LiHzS was studied at
temperatures from 78°K to 463°K. The spectrum observed at 78°K does not reflect any motion within the hydrazine group and will be discussed in this chapter. The spectrum at higher temperatures reflects motion and will be discussed in Chapter III within the context of other measurements which have to do with motion of the deuterons in the crystal.

In first order the interaction between the nuclear quadrupole moment of the deuteron and the electric field gradient (efg) at the site of the deuteron splits the deuteron NMR line into two lines spaced equally above and below the position of the unperturbed line.* Since there are twenty deuterons in a unit cell, for arbitrary orientation of the crystal relative to the applied dc magnetic field $H_0$, the spectrum consists of forty lines. However, there are only five sites which are chemically non-equivalent. For example, the deuteron at site 1 of any one of the four hydrazine groups of a unit cell interacts with an efg possessing the same components as each of the three other site 1 deuterons of the cell. The four site 1

*Appendix A contains a discussion of the nuclear quadrupole interaction and the technique of nuclear magnetic resonance spectroscopy employed in the determination of the efg tensor carried out in this study.
deuterons differ only in the direction of the axes of the coordinate systems in which their respective efg tensors are diagonal. A result of this chemical equivalence and of the crystal symmetry (see Fig. 1) is that if the field \( H_0 \) is made perpendicular to one of the crystal axes, at most ten pairs of lines are observed. With \( H_0 \) parallel to a crystal axis only five pairs of lines are observed.

Spectra were obtained at 2° intervals about the three crystal axes. Fig. 4 displays typical spectra obtained at 77°K. The data was analyzed in the following fashion. First the position of the spectral lines relative to the center of the spectrum was measured directly from the recorder chart and expressed in gauss since the experiment was done at fixed frequency. For many crystal orientations the individual spectral lines were not all distinguishable. This is shown clearly in Fig. 4b where, of the ten pairs of lines which should be discernible, five pairs are merged with the other five. The line positions were then plotted against the orientation angle, \( \phi \), of the crystal relative to \( H_0 \). These plots were rough fit by using a set of sine curve overlays. By using this rough fit it was possible to exclude data points having large error. The remaining points were used in a least squares computer program to calculate the curve.
Fig. 4-a. 77°K Spectrum, Crystal Oriented 10° from $a \parallel H_0$ with $c \perp H_0$.

Fig. 4-b. 77°K Spectrum, Crystal Oriented 27° from $a \parallel H_0$ with $c \perp H_0$. 
which best fit the data. Figs. 4, 5, and 6 are plots of the quadrupole splitting curves for the five deuteron sites for rotations about the three crystal axes.

In the case that the efg tensor is cylindrically symmetric, a rotation about an axis perpendicular to the principal axis of the efg tensor makes $2\Delta\nu$ proportional to $(1 + 3 \cos 2\theta)$ where $\theta$ measures the angle between the principal axis and the magnetic field $H_0$. $2\Delta\nu$ then ranges between a maximum positive value for $\theta=0$, and a maximum negative value at $\theta=90$. The negative value is just half the positive value in absolute magnitude. A rotation about an arbitrary axis includes the orientation $H_0$ perpendicular to the principal axis, although it does not include $H_0$ parallel to the principal axis. By examination of the plots of $2\Delta\nu$ (Figs. 5, 6, and 7) it can be seen that the negative maximum values are approximately the same independent of the rotation axis. This indicates the nearly cylindrical symmetry of the bonds studied. The values of the components of the efg tensor relative to the crystal axes are obtained from the $A$, $B$ and $C$ of Eq. 2.1. The efg tensor was then diagonalized and values of the coupling constant, the asymmetry parameter, and the angles
relating principal axes of the efg tensor to the crystal set were obtained. This data is given in Table II.

The estimated errors included in Table II are based on the following considerations. One source of error is misalignment of the crystal in the spectrometer head, so that the rotation axis is not quite parallel to a crystal axis. The agreement between the spectra obtained during rotations about different axes but with the same crystal axis presumably parallel to \( H_0 \) was used to check the alignment. Such checks indicated that initial alignment of the crystal was accurate to better than \( \frac{1}{2}^0 \). The rotation angle was read directly to \( 1^0 \) and estimated to \( 0.1^0 \). Error in the rotation angle is believed to be less than \( 0.1^0 \). The data points included in Figs. 5, 6 and 7 are those finally used in the least squares calculation of the curves. To test the effect of errors on the values of the efg tensor components in the principal axis system a set of varied data was fed into the diagonalization program and the estimates of error were based on the resulting variation in the output.

DISCUSSION.

The deuteron efg results are related to the LiHgS structure. (See Appendix C)
Fig. 5 Quadrupole Splitting Patterns for Rotation about the a Crystallographic Axis at Liquid Air Temperature.
Fig. 6 Quadrupole Splitting Patterns for Rotation about the b Crystallographic Axis at Liquid Air Temperature.
Fig. 7  Quadrupole Splitting Patterns for Rotation about the c Crystallographic Axis at Liquid Air Temperature.
TABLE II

Coupling Constant eqQ/h, Asymmetry Parameter \( \eta \), and the Angle Formed Between the Principal Axis of the efg Tensor and the Crystal Axes, for the Deuteron Sites Indicated in Fig. 1. Also Listed Is the Angle Formed Between the Principal Axis of the Field Gradient and the Vector Between the Nitrogen and Proton Involved in the Bond. (All Estimated Errors for Angles Given Are \( \pm 1^\circ \)).

<table>
<thead>
<tr>
<th>Temp. ( \theta K )</th>
<th>Bond</th>
<th>( \text{eqQ/h kHz} )</th>
<th>( \eta )</th>
<th>( \theta_x )</th>
<th>( \theta_y )</th>
<th>( \theta_z )</th>
<th>( \phi_{zz} ), N-H Angle, deg.</th>
</tr>
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<td>77</td>
<td>1</td>
<td>208 ( \pm ) 1</td>
<td>0.16 ( \pm ) 0.07</td>
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<td>19</td>
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<td>0.12 ( \pm ) 0.07</td>
<td>114</td>
<td>6</td>
<td>155</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>166 ( \pm ) 1</td>
<td>0.05 ( \pm ) 0.07</td>
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<td>162</td>
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<td>10</td>
</tr>
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<td></td>
<td>4</td>
<td>167 ( \pm ) 1</td>
<td>0.10 ( \pm ) 0.07</td>
<td>114</td>
<td>4</td>
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<td>0.05 ( \pm ) 0.07</td>
<td>8</td>
<td>70</td>
<td>131</td>
<td>1</td>
</tr>
<tr>
<td>193</td>
<td>1</td>
<td>201 ( \pm ) 1</td>
<td>0.15 ( \pm ) 0.07</td>
<td>108</td>
<td>20</td>
<td>98</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>178 ( \pm ) 1</td>
<td>0.08 ( \pm ) 0.07</td>
<td>114</td>
<td>5</td>
<td>155</td>
<td>4</td>
</tr>
</tbody>
</table>
next largest components of the efg tensor will be denoted as first principal and second principal axes respectively. As can be seen from Table II, the first principal component lies nearly along the N-H bond direction at each deuteron site. The angle so formed ranges from 10° for bond 5 to about 100° for bonds 1 and 3. (See Table III for bond lengths.)

If the angles formed between the efg principal axis direction and the crystal axes for one of the five sites of the unit cell are denoted \( \theta_x, \theta_y, \) and \( \theta_z \), then the three symmetry related sites of the cell have the corresponding angles, \( \theta_x, \pi-\theta_y, \theta_z; \pi-\theta_x, \theta_y, \theta_z; \pi-\theta_x, \pi-\theta_y, \theta_z \). This makes the efg tensor principal axis of site 1 of molecule 1 and site 3 of molecule 4 almost parallel and site 2 of molecule 1 and site 4 of molecule 4 nearly parallel. These similarities would make the assignment of efg tensors to bond sites ambiguous on the basis of structure alone. Fortunately, the evidence that the deuterons of sites 3, 4 and 5 undergo hindered rotation makes it possible to assign the efg tensors of sites 1 and 2 at 193°K where the NMR spectra of the sites 3, 4, and 5 are merged.

The second principal component is found to lie approximately along the normal to the plane defined by \( N_1-N_2-D \). The angles formed between the second principal component...
and the normal to the plane of \( N_1-N_2-D \) are 17°, 16°, 14°, 12° and 5° for sites 1 through 5 respectively. The estimated error is ±3°, somewhat larger than for the first principal component because the efg tensors are nearly axially symmetric. Similar results have been found by Chiba (17) for the O-D...O bond. The slight change in the efg tensor orientation of the 1 and 2 site deuterons between 77°K and 193°K is smaller than the experimental error.

The spectrum observed at an orientation with \( c \perp H_0 \) and near \( b \parallel H_0 \) showed some evidence of a splitting of the lines corresponding to site 1. This may indicate that the deuteron of site 1 can be found at either of two almost identical positions. The only region of the rotation spectrum in which this splitting was evidenced is that corresponding to maximum splitting, for which the field \( H_0 \) is almost along the first principal axis of the field gradient tensor.

It was assumed that such a splitting might be associated with structural differences corresponding to ferroelectric domains in the crystal. Ordinarily the domains of opposite polarization of a ferroelectric are related by reflection. Observation of such a splitting as described would indicate that in LiHzS domains are not
related by reflection and might be considered a new type of ferroelectric. (14) An unsuccessful attempt was made to observe the effect of electric fields, of the order of \(10^4\) \(v/m\), on the spectrum. The crystal was prepared by cutting and polishing faces perpendicular to the \(c\) axis. Silver contacts were then painted on these faces in the form of \(E\) in order to minimize rf currents. The signal to noise ratio was so degraded, by the introduction into the sample region of these polarizing plates, that the line splitting was no longer observed. The low temperature spectrum showed no other evidence of domain effects.

A sufficiently large number of hydrogen bonded systems of the type \(O-H\ldots O\) have been studied to allow correlation of the coupling constant \(\epsilon_Q/h\), with \(O\ldots O\) bond lengths and with the \(O\ldots H\) stretching frequencies \(\nu_{OH}\). (18) The number of similar studies of \(N\ldots H\ldots X\) systems is small. Table IV lists the coupling constant and other pertinent information for several such systems.

\(O\ldots O\) bond lengths range from 2.40 \(\AA\) to about 3 \(\AA\). The range \((26)\) of \(N\ldots O\) bond lengths is approximately 2.85 \(\AA\) to 3.05 \(\AA\).* Although a plot of \(\epsilon_Q/h\) against bridge length

---

*These estimates do not include weak or bifurcated bonds for which the bridge length may be considerably longer.
TABLE III
N-H...X Bond Angles and Intra-bond Lengths Calculated
from the Room Temperature Data of Padmanabhan and
Balasubramanian.(11)

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for O...O bonds shows a strong correlation, an attempt to
correlate bridge length with eqQ/h for N-H...O bonds was
not successful. Within the ND₃ group of LiDzS the
dependence of eqQ/h on \((1/r_{N-D})^3\) is consistent. The
slope of such a plot can be used to estimate the effective-
charge of the nitrogen nucleus in the crude approximation
that no other nuclear site contributes to the efg at the
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<th>Compound</th>
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<th>Temperature</th>
<th>eqQ/H (kHz)</th>
<th>n</th>
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<td>0.139±0.010</td>
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<td>0.146±0.010</td>
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<td>206.3±1.2</td>
<td>0.138±0.010</td>
<td>19</td>
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<tr>
<td>Urea d₄ single crystal</td>
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<td>75°K</td>
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<td>N-D...0</td>
<td>180°K</td>
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<td>0.0</td>
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Fig. 8. Coupling Constant Plotted Against the Square of the X-H Stretching Frequency for O-H Bonds of a Number of Compounds Except for the N-H Bonds of LiHzS as Indicated. (After Blinc & Hadzi)(18)

deuteron. Such an estimate yields a value of 0.45e for the effective nuclear charge of the nitrogen.

Fig. 8 shows a plot of eqQ/h against the square of
the O-H and N-H\textsuperscript{(27,28)} stretching frequencies. Bonds represented in the upper right region of the plot are O-H...O bonds of crystal hydrates, while the O-H...O bonds found in phosphates and selenites are represented in the lower left region. The stronger bonds of the crystal hydrates show a larger dependence on $v\text{\textsubscript{OH}}^2$ than the bonds of the phosphates and selenites. The points corresponding to the nitrogen-hydrogen bonds of LiHzS fall near the transition between the two general O-H bonds represented in this plot.
CHAPTER III  DEUTERON MOTION

CONDUCTIVITY AND DIELECTRIC CONSTANT.

An electrolysis experiment carried out by Vanderkooy demonstrates that the c axis conductivity in LiHzS is due to protons. Electrical conductivity measurements by Vanderkooy, Cuthbert and Petch (29) (hereafter referred to as VCP) show that the c axis conductivity is two to three orders of magnitude greater than conductivity in the a or b direction. Their experiments were carried out on crystal samples of approximately 8 mm thickness with electrodes of area about 0.5 cm². A dc voltage of 290 volts was applied to the sample and an electrometer was used to measure the current. Although care was taken to avoid measuring polarization currents by waiting a time after application of the voltage before measuring the current, no mention is made of the use of a guard ring circuit in the experiment. Values found for the conductivity in the a, b and c axis directions are given in Table V. The c axis conductivity as a function of temperature found by VCP is displayed in Fig. 9. It was found that the a and b axis conductivities could not be represented by a single activation energy over this temperature range.

The conductivities of LiHzS and LiDzS reported herein have been measured by a slightly different technique. The
experiment is described in Chapter IV. The room temperature conductivities for deuterated and undeuterated crystals are given in Table V. Activation energies are also given. These are somewhat lower for LiHzS than those found by VCP. In addition the a and b axis conductivities of the
deuterated compound were measured. Although they could not be described by a single activation energy over the entire temperature range studied, the data between room temperature and about 110°C appeared linear and was best fit to get an estimate of the activation energy for this region. Two a axis and one b axis studies were used, giving the activation energies indicated in Table V. Above 170°C all three of these log conductivities vs 1/T curves indicate activation energies of more than 1.5 eV. The c axis log conductivity vs 1/T curve has a constant slope over the entire temperature range and the best fit to this is shown in Fig. 9.

The dielectric constant of LiDzS has been measured in this laboratory. The results of these measurements are displayed in Figs. 10, 11 and 12. Pepinsky et al, (10) who first examined the dielectric constant of the crystal, found no anomaly in the dielectric constant between -196°C and 140°C. Our study has shown no dielectric peak up to 205°C.

According to the Debye* equations $\varepsilon' = 1/(1 + \omega^2 r^2)$ and $\varepsilon'' = \omega r/(1 + \omega^2 r^2)$. Log $\varepsilon'$ and log $\varepsilon''$ plotted as

Fig. 9. Best Fit Curves of the Logarithm of Conductivity for LiHzS and LiDzS as a Function of Temperature. (VCP Indicates Results from Reference 29.)
Fig. 10. Logarithm of the Real and Imaginary Parts of the Dielectric Constant for LiHzS and LiDzS Measured Along the c Axis vs Frequency at which the Measurement Was Made.
functions of $\omega$ for several fixed temperatures show negative slopes near -0.5, as shown in Fig. 10. This behavior is not consistent with the Debye equations, which result from the assumption of a single relaxation time $\tau$. It agrees quite well with the assumption of a distribution $y(\tau)$ of relaxation times in the relations

$$
\varepsilon' = \varepsilon_\infty + \frac{\int_0^\infty y(\tau)d\tau}{1 + \omega^2\tau^2},
$$

$$
\varepsilon'' = \frac{\int_0^\infty \omega \tau y(\tau)d\tau}{1 + \omega^2\tau^2},
$$

if $y(\tau) = (a-1)\tau_m^{a-1}[\varepsilon(0)-\varepsilon_\infty] \tau_m^{a-1}$ for $0 < \tau < \tau_m$, and $y(\tau) = 0$ for $\tau > \tau_m$. For this $y(\tau)$, if $\omega\tau_m > 1$, the dielectric constant becomes

$$
\varepsilon = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\pi(a-1)[\varepsilon(0)-\varepsilon_\infty]}{2(\omega\tau_m)^2} \left[ \frac{1}{\sin(a\pi/2)} - j \frac{\sin((a+1)\pi/2)}{\sin((a+1)\pi/2)} \right].
$$

The Cole-Cole plot of $\varepsilon''$ versus $\varepsilon'$ in Fig. 11 shows that LiDzS almost obeys this expression at 25°C for $a = 0.5$.

A more concentrated distribution of relaxation times is exhibited by the curve for LiHzS at room temperature, for which the contribution $\sigma_{dc}/\varepsilon_0\omega$ to $\varepsilon''$ made by the dc conductivity mechanism has been subtracted out. A single relaxation time would give a semicircle centered on the $\varepsilon'$ axis.

Activation energies for the relaxation mechanism are estimated from Fig. 12. For the deuterated compound two contributions are evident, a low temperature contribution of 0.4 eV and a contribution of 0.7 eV in the temperature region above 100°C.
Fig. 11. $\varepsilon''$ vs $\varepsilon'$ for LiH$_{2}$S and LiD$_{2}$S.
Fig. 12. Logarithm of the Real and Imaginary Parts of the Dielectric Constant for LiHzS and LiDzS Measured Along the c Axis as a Function of Temperature.
Two previous NMR studies have been carried out on LiH₂S. In the first of these, the second moment of the protons and the quadrupolar splitting of Li⁷ were measured. In the later work, the second moment measurements of the first work were extended and the spin lattice relaxation time of the protons was measured. The first study of the second moment was carried out before the neutron structure study was done. On the basis of the second moments measured at various temperatures in powder samples and in single crystals at various orientations, the arrangement of the protons was deduced and the NH₃ and NH₂ motions were hypothesized. Fig. 13 shows the proton second moment as a function of temperature along the Li⁷ satellite separation. Because of the change in the satellite separation, Cuthbert and Petch suggest that the crystal undergoes a gradual structural change which is complete at about 165°C.

The reduction in the second moment between liquid air temperature and 80°C was attributed to the onset of hindered rotation of the NH₃ group. The further reduction between 20°C and 150°C was thought due to whatever mechanism provided exchange between sites 1 and 2. The final drop in second moment to the very low value of about 0.5 gauss at 200°C.
Fig. 13. The Open Circles Give the Variation with Temperature of the Frequency Separation Between the Two Li7 Satellites Which Occur on the Same Side of the Central Line and Coincide in the High Temperature Polymorph of Lithium Hydrazinium Sulfate. The Solid Circles Give the Variation with Temperature of the Second Moment of the Proton Resonance in Powdered LiHzS. (After Reference 12)
was thought to be due to either rapid diffusion of the protons through the crystal or to tumbling of the entire \( \text{N}_2\text{H}_5 \) group. These authors suggest that the ferroelectric property of the crystal is associated with ordering of the N-H...N-H... chains (Fig. 2). It was then pointed out that on the basis of this model, exchange between sites 1 and 2 would lead to a loss of order of these N-H dipoles and hence a ferroelectric transition.

The second moment measurements presented in the later study are in general agreement with those of the earlier, although the knee in the curve at about 8.8 gauss\(^2\) was not repeated (Fig. 14). The spin lattice relaxation time of the protons was measured. Fig. 15 shows a plot of \( T_1 \) vs 1/T. Below a temperature of about 190°K the relaxation is attributed to molecular reorientation of the \( \text{NH}_3 \) group with activation energy 0.182 ± 0.013 eV. It is assumed that above about 60°C the \( \text{NH}_2 \) reorientation mechanism is responsible for the decrease in \( T_1 \) and the activation energy is found to be 0.43 ± 0.09 eV.

In summary, the second moment studies of the protons suggest that the protons of sites 3, 4 and 5 undergo a hindered rotation, and that this motion becomes important in the temperature range between 100 and 150°K. The protons of sites 1 and 2 begin to undergo some sort of
Fig. 14. Temperature Dependence of the Second Moment of the Proton Absorption Signal from Powdered LiHzS. (After Reference 13)

exchange between sites in the region near 0°C. Above 150°C either a very rapid diffusion of protons between N₂H₅ groups starts to occur or else the groups themselves begin to tumble and translate through the crystal. The T₁ measurements yield activation energies for the rotations. Li⁷ quadrupolar splitting studied as a function of
Fig. 15. Temperature Dependence of the Proton Spin Lattice Relaxation Time $T_1$ in Lithium Hydrazinium Sulfate. (After Reference 13)

temperature implies a structural change to a higher symmetry form which is complete near $165^\circ$C.
HIGH TEMPERATURE SPECTRUM.

If the quadrupolar interaction is a perturbation on the Zeeman interaction as in these experiments, when a deuteron changes sites its energy level scheme is changed if there is a change in the electric field gradient component parallel to \( H_0 \). When the rate of site change becomes large enough, the spectral lines corresponding to individual sites are broadened and disappear. If the exchange frequency becomes higher still, a new pair of spectral lines may appear, corresponding to an efg which is the average over the sites between which the jumping occurs.

Evidence discussed in the previous section indicates that protons in the \( \text{NH}_2 \) and \( \text{NH}_3 \) sites undergo hindered rotation. By studying the NMR spectra of deuterons in LiDzS it has been possible to determine unambiguously the type of motion taking place, along with estimates of the frequency of the motion, and the activation energies involved.

When the deuteron NMR spectrum (Fig. 16) of LiDzS is studied as a function of temperature it is found that the lines in a spectrum corresponding to sites 3, 4, and 5 broaden and vanish near \( 110^0\text{K} \). As the temperature is further increased a new pair of lines appear near \( 140^0\text{K} \). These lines are very strong and are still in evidence at \( 465^0\text{K} \). The splitting of these lines as a function of the
Fig. 16. NMR Spectra Taken with $b \parallel H_0$ at Temperatures Indicated.
Fig. 17 Quadrupole Splitting Patterns of the Two Sets of Averaged Lines for Rotation about the a Crystallographic Axis at 95°C. Dashed Lines Indicate Regions in which the Spectral Lines Could not be Observed.
Fig. 18 Quadrupole Splitting Patterns of the Two Sets of Averaged Lines for Rotation about the b Crystallographic Axis at 95°C. Dashed Lines Indicate Regions in which the Spectral Lines Could not be Observed.
Fig. 19 Quadrupole Splitting Patterns of the Two Sets of Averaged Lines for Rotation about the c Crystallographic Axis at 95°C. Dashed Lines Indicate Regions in which the Spectral Lines Could not be Observed.
angle between crystal axis and magnetic field is shown in Figs. 17, 18, and 19. Near 285°C, the lines in the spectrum corresponding to sites 1 and 2, broaden and disappear. A new pair of lines, due to the average of sites 1 and 2, appears at about 330°C. These lines, however, are not evident for all orientations of the crystal relative to \( H_0 \). Figs. 17, 18 and 19 show the splitting for these lines, indicating as well the angular region in which the lines are not observed.

The complete rotation spectrum of the deuterons was studied at 193°C, 298°C, 338°C, 368°C, and 438°C. Because the spectrum is not sensitively dependent on the temperature, a variation of ±5°C was allowed. This produced variations in the spectrum well within experimental error. The results of these measurements are tabulated in Table VI.

The values of \( \text{eqQ}/h \) for the averages over sites 3, 4, and 5 show a consistent decrease of about 10% from -80°C to 165°C. If all the contents of the unit cell were to expand at the same rate, the efg would vary as \((\text{lattice parameter})^{-3}\). Using the average of the anisotropic thermal expansion coefficients, this temperature yields an efg decrease of about 2.5% from -80°C to 165°C. Two possible origins for the remainder of the decrease are the increase with temperature in the amplitude of the torsional
### TABLE VI

Coupling Constant $\text{eqQ/h}$, Asymmetry Parameter $n$, and the Angles Between the First Principal Axes and the Crystallographic Axes for the $\text{efgs}$ Resulting from Motional Averaging over Sites 1 and 2 and over Sites 3, 4 and 5. Calculated Averages Based on $\text{efgs}$ Measured at $78^\circ\text{K}$ for Individual Sites Are Given for Comparison.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>eqQ/h, kHz</th>
<th>$n$</th>
<th>$\theta_x$</th>
<th>$\theta_y$</th>
<th>$\theta_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80°C</td>
<td>48.9 ± 0.5</td>
<td>0.29 ± 0.05</td>
<td>37.1</td>
<td>127.4</td>
<td>89.0</td>
</tr>
<tr>
<td>Measured for average due to sites 3, 4 and 5</td>
<td>48.6 ± 0.5</td>
<td>0.22 ± 0.05</td>
<td>38.0</td>
<td>127.5</td>
<td>89.9</td>
</tr>
<tr>
<td>25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65°C</td>
<td>47.5 ± 0.5</td>
<td>0.18 ± 0.05</td>
<td>38.4</td>
<td>128.3</td>
<td>88.4</td>
</tr>
<tr>
<td>95°C</td>
<td>46.3 ± 0.5</td>
<td>0.16 ± 0.05</td>
<td>39.1</td>
<td>129.0</td>
<td>87.6</td>
</tr>
<tr>
<td>165°C</td>
<td>44.0 ± 0.5</td>
<td>0.20 ± 0.05</td>
<td>40.1</td>
<td>130.0</td>
<td>87.5</td>
</tr>
<tr>
<td>Calculated average for sites 3, 4 and 5</td>
<td>51.0</td>
<td>0.46</td>
<td>36.9</td>
<td>126.7</td>
<td>88.5</td>
</tr>
<tr>
<td>Measured for average due to sites 1 and 2</td>
<td>91.0 ± 3</td>
<td>0.90 ± 0.15</td>
<td>64.0</td>
<td>52.0</td>
<td>131.0</td>
</tr>
<tr>
<td>95°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>165°C</td>
<td>89.4 ± 3</td>
<td>0.75 ± 0.15</td>
<td>64.1</td>
<td>61.3</td>
<td>139.5</td>
</tr>
<tr>
<td>Calculated average over sites 1 and 2</td>
<td>97.8</td>
<td>0.98</td>
<td>64.2</td>
<td>45.8</td>
<td>124.8</td>
</tr>
</tbody>
</table>
oscillations of the ND$_3$ groups, and the structure change indicated by the decrease in the difference between the quadrupolar splittings of the two Li$^7$ sites. The direction of the first principal axis of the ND$_3$ group average forms an angle of 3.6° at room temperature, 2.6° at 95°C and about 1° at 165°C with the $N_1$-$N_2$ direction as calculated from the neutron diffraction data obtained at room temperature.

A somewhat similar ND$_3$ group has been studied in glycine (Table IV). This group is of the form C-ND$_3$ as opposed to the N-ND$_3$ found in LiDzS. The coupling constant for the glycine ND$_3$ average is between 70 and 80 kHz as compared to 48.6 kHz in LiDzS at 25°C. The asymmetry parameter for the group in glycine is 0.22 as compared to 0.22 ± 0.05 in LiDzS. This would suggest that either the effective charge of the nitrogen in a N-N bond is less than that in an N-C bond or that the N-D distances are greater in LiDzS than in glycine, or a combination of these two.

The efg resulting from motional averaging over bonds 1 and 2 did not change measurably between 65 and 95°C. The efg at 165°C showed a change and its coupling constant, asymmetry parameter, and angles are given in Table VI. Because of the limited angular range over which these lines could be observed, the estimated error is larger than for
the D$_3$-D$_4$-D$_5$ average. At 95°C the first principal axis of
the D$_1$-D$_2$ average lies within 2° of the plane defined by
H$_1$-N$_1$-H$_2$ and within 4° of the line bisecting the H$_1$-N$_1$-H$_2$
angle.

Values of the coupling constant, asymmetry parameter,
and the angles between the first principal axis and the
crystal axes are given in Table VI for a calculated average
over sites 1-2 and over sites 3-4-5. This calculated
average is obtained from an efg whose components in the
crystal frame are the sums of the components of the efg
tensors for the individual sites in the crystal frame,
divided by the number of sites. The agreement between the
calculated averages and the values obtained at lowest
temperature measured is good. The type of motion which
gives rise to these averages can be understood from the
measurements discussed above. The ND$_3$ exchange takes place
symmetrically about the N-N axis by means of hindered
rotation through 120° steps as was suggested by Cuthbert
and Petch(12). The D$_1$, D$_2$ averaging takes place by
interchange between sites 1 and 2 bonded to the same
nitrogen. This does not indicate a rotation about the N-N
bond direction as had previously been suggested as a
possible motion.(13)
EXCHANGE PROBABILITY.

Abragam (8) discusses a general method for calculating the exchange probability per unit time, $\omega$, for nuclear exchange between sites from a knowledge of the line width. Since in principle the technique is applicable to the case of jumping between any number of nuclear sites, it is possible to estimate the exchange probability as a function of temperature and also the activation energy for the exchange of deuterons of both ND$_2$ and ND$_3$ sites. Chiba (31) has applied a similar method to the case of D$_2$O in Ba(ClO$_3$)$_2$·D$_2$O.

The calculation of the relation between intersite exchange probability and line width is based on the following assumptions. The probability that the Larmor frequency of the nucleus, $\omega$, has a value $\omega_2$ at the time $t'$ = $t + \Delta t$ when it is known that it had a value $\omega_1$ at time $t$ is:

1. independent of the values of $\omega$ prior to $t$
2. dependent on the times $t$ and $t'$ only through the difference $t' - t = \Delta t$ and can accordingly be written as $W(\omega_1|\omega_2,\Delta t)$.

The absorption

$$I(\omega) = \text{re} \int_0^\infty G(t)e^{-i\omega t}dt$$ (3.1)

is obtained by calculating the relaxation function
It is found that
\[ G(t) = \mathbf{W} \cdot \exp\{(i\mathbf{w} + \pi)t\} \cdot \mathbf{T}, \]  
which makes
\[ I(\omega) = \text{re}\{\mathbf{W} \cdot A^{-1} \cdot \mathbf{T}\}. \]  

\( W \) is a vector whose components, \( W_\alpha \), are the probabilities that at any time \( t \) the frequency of the system is \( \omega_\alpha \). \( A^{-1} \) is the inverse of the matrix
\[
A = i(\mathbf{w} - \omega I) + \pi 
\]  
where \( \mathbf{w} \) is a diagonal matrix with components \( (\omega)_\alpha = \omega_\alpha \delta_{\alpha \beta} \), \( (\pi)_\alpha \beta = \pi(\omega_\alpha, \omega_\beta) \) the probability of transition between levels \( \omega_\alpha \) and \( \omega_\beta \), \( \mathbf{T} \) a unit matrix, and \( \omega \) a constant. \( A \) is of rank \( n \) where \( n \) is the number of deuteron sites among which jumping occurs. The matrices
\[
\mathbf{\pi} = \begin{pmatrix} \Omega^- & \Omega \\ \Omega & -\Omega \end{pmatrix} 
\]  
and
\[
\mathbf{\omega} = \begin{pmatrix} \omega + \delta & 0 \\ 0 & \omega - \delta \end{pmatrix} 
\]  
where \( 2\delta \) is the line separation (see Fig. 20) give for the
Fig. 20. Ideal and Observed D₃ and D₂ NMR Spectra.
ND\textsubscript{2} case

\[
A = \begin{pmatrix}
  i(\omega + \delta + i\Delta) - \Omega & \Omega \\
  \Omega & i(\omega - \delta + i\Delta) - \Omega 
\end{pmatrix}, \quad (3.8)
\]

where \( \Delta \) is the unbroadened line width.

The resulting absorption for the ND\textsubscript{2} case is

\[
I(\omega) = \text{re} \{ \frac{i \Gamma (-\omega + \delta - i\Delta) - (\omega + \delta + i\Delta) - 4\Omega}{(\delta^2 + \Delta^2 - \omega^2) - 2\Delta\Omega + 2i\omega(\Omega - \Delta)} \}. \quad (3.9)
\]

For the ND\textsubscript{3} case the matrices

\[
\bar{\pi} = \begin{pmatrix}
  -\Omega & \Omega/2 & \Omega/2 \\
  \Omega/2 & -\Omega & \Omega/2 \\
  \Omega/2 & \Omega/2 & -\Omega 
\end{pmatrix}, \quad (3.10)
\]

and

\[
\bar{\omega} = \begin{pmatrix}
  \omega + \delta & 0 & 0 \\
  0 & \omega & 0 \\
  0 & 0 & \omega - \delta 
\end{pmatrix}, \quad (3.11)
\]

yield

\[
A = \begin{pmatrix}
  i(\omega + \delta + i\Delta) - \Omega & \gamma & \gamma \\
  \gamma & i(\omega + i\Delta) - \Omega & \gamma \\
  \gamma & \gamma & i(\omega + \delta + i\Delta) - \Omega 
\end{pmatrix}. \quad (3.12)
\]
$\Delta$ is the unbroadened line width and $\gamma = \omega/2$. The absorption is then calculated to be

$$I(\omega) = \text{re} \left\{ \frac{3i\omega(\Omega+2\Delta)-3\Omega\Delta-(3\Omega/2)^2-\delta^2+3\omega^2-3\Delta^2}{i[-\omega^2+3\omega\Delta^2+\omega\delta^2+(9/4)\Omega^2\omega+6\Omega\omega\Delta]+[3\omega^2\Delta^2-\Delta^3-\delta^2\Omega+3\omega^2\Delta^2]} \right\}.$$  

The low temperature spectrum observed for the ND$_2$ group consists of two lines split by 75 kHz (Fig. 20). For the ND$_3$ group three lines are involved and the line separation is indicated in Fig. 20. $I(\omega)$ is approximated for two limiting cases, $\Omega<<\delta$ (low temperature) and $\Omega>>\delta$ (high temperature) and from the resulting relations the line width is identified.

The ND$_2$ line widths are:

$$W_{LT} = \Omega + \Delta \quad \text{Low Temperature}$$
$$W_{HT} = (\frac{\delta^2}{2\Omega}) + \Delta \quad \text{High Temperature}$$

The ND$_3$ line widths are:

$$W_{LT} = \Omega + \Delta \quad \text{Low Temperature}$$
$$W_{HT} = 4/9 \frac{\delta^2}{\Omega} + \Delta \quad \text{High Temperature}$$
These expressions are then solved for $\Omega$. The line width value, $W$, is obtained by measuring the signal to noise ratio $(S/N)$ as a function of temperature. The line width is assumed to be the reciprocal of the quantity $C(T/T_0)(S/N)$ where $T/T_0$ compensates for the decrease in population difference and hence $S/N$ with increasing temperature $T$. For the $\text{ND}_2$ group the constant $C$ is obtained from the value $(2.3 \times 10^4/\text{sec}^{-1})$ of the line width at a temperature low enough to insure no line broadening due to the motion of interest. The width of the merged line is approximately the same so the same value of $C$ is used for both the high and low temperature cases. The line width for the $\text{ND}_3$ group merged lines is larger $(3.9 \times 10^4/\text{sec}^{-1})$ than that for the unmerged lines so a different value of $C$ was used for the high temperature than for the low temperature. The value of $\delta$ used in the calculation for $\text{ND}_3$ group was obtained by taking the average of the separation of the three unmerged lines giving $\delta = 110$ kHz. The value of $\delta$ used in the calculation for the $\text{ND}_2$ group was taken to be half the splitting of the two unmerged lines (see Fig. 20). The resulting values of $\Omega$ are plotted against $1/T$ in Figs. 21, 22. The $\text{ND}_2$ data for the unmerged and merged regions is fitted to the line shown yielding an activation energy for the $\text{ND}_2$ motion $E_a = .46 \text{eV}$. 
Fig. 21. Temperature Dependence of the Exchange Probability $\Omega$ for Exchange Between Deuteron Sites 1 and 2.
Fig. 22. Temperature Dependence of the Exchange Probability $\omega$ for Exchange Between Deuteron Sites 1, 2 and 3.
The ND₃ data for the merged lines shows a much steeper slope than for the unmerged region. The straight line shown in Fig. 22 corresponds to an activation energy of 1.19 eV, and approximates a best fit to the data shown.

The method discussed in this section is not as dependable a technique for determining the activation energy for such motion as is the measurement of the deuteron spin-lattice relaxation time, T₁. The slope of the curve ε versus 1/T is dependent on both the line splitting δ and the line width Δ. The value chosen for δ is unambiguous only if the splitting is such that the averaged line falls on the real average of the positions of the unmerged lines. In the case of the ND₃ motion the idealized spectrum and the real spectrum differ markedly (see Fig. 20). The primary advantage of this type of measurement is that it may provide an estimate of the activation energy for a particular motion on the basis of a much less complex and expensive apparatus than is required for T₁ measurements.

DEUTERON SPIN-LATTICE RELAXATION.

The spin-lattice relaxation time T₁ for deuterons in LiD₂S was measured by a double 90° pulse technique. The
first pulse is applied to the system in equilibrium and the nuclear response a given time after the end of the pulse has a magnitude $S_0$. The second pulse is separated from the first pulse by a time $t$. The response $S(t)$ to the second pulse was measured and fitted to the relation

$$S_0 - S(t) = S_0 e^{-t/T_1}.$$  (3.14)

It can be shown* that for the three level deuteron system $(m = -1, 0, +1)$, Eq. (3.14) holds only for the experiment carried out with the lines corresponding to transitions between $m = (0 \leftrightarrow +1)$ and $m = (-1 \leftrightarrow 0)$ merged so that the population differences between the $m = 0$, $m = 1$ and $m = 0$, $m = -1$ levels are symmetrically reduced to zero. The equilibrium populations are then re-established with a single time constant, $T_1 = (P_1 + 2P_2)^{-1}$, where $P_1$ and $P_2$ are the probabilities for a $\Delta m = 1$ and $\Delta m = 2$ transition respectively.*

Fig. 23 shows the values of $1/T_1$ obtained by this method plotted against $1/T$. Because of the complexity of the spectrum in the region below $0^\circ C$ it was not possible to carry out the experiment on the ND$_3$ lines at a crystal

*Appendix B contains a development of the equations pertinent to this section.
Fig. 23. Temperature Dependence of the Deuteron Spin-Lattice Relaxation Time.

$\frac{1}{T_1} \times 10^3 \text{ sec}^{-1}$

$10^3/T(0K)$

$\triangle \text{ ND}_3 \ a \parallel H_0$

$\circ \text{ ND}_3 \ 17^\circ \text{ from } a \parallel H_0$

$n \text{ ND}_2 \ a \parallel H_0$
orientation for which the line splitting was zero. Attempts
to do so resulted in erroneous response, because the Fourier
spectrum of the 90° pulse contained components at the fre-
quency of neighboring lines and consequently the response
was modulated at a frequency determined by the separation
between these lines. The same problem was encountered when
measurements of $T_1$ for the ND$_2$ lines were attempted at the
zero crossings. Consequently the ND$_2$ and low temperature
ND$_3$ experiments were done with the crystal oriented with
a $\parallel H_0$

The experimental results for a $\parallel H_0$ and for the
transition $m = -1$ to $m = 0$ appear to depend on only a
single relaxation time which is taken to be the experimental
$T_1$. The values of $T_1$ measured (Fig. 23) for the orientation
a $\parallel H_0$ were obtained by saturating the $m = 0$ to $m = -1$
transition and analyzing the response to determine this
single relaxation time $T_1$. The theoretical response* for
the experiment in which only one of the transitions is
saturated is

$$S_0 - S(t) = \frac{1}{4} S_0 \left[ 3 \exp(-3P_1)t + \exp(-(P_1 + 2P_2)t \right].$$  (3.15)

*Appendix B contains a development of the equations
pertinent to this section.
TABLE VII

Values of Electric Field Gradient Tensor Components in the Crystal System Multiplied by $K = 3eQ/2h$, in kHz, for the Five Deuteron Sites in Li$N_2D_5SO_4$.

<table>
<thead>
<tr>
<th>Site</th>
<th>$K_{XX}$</th>
<th>$K_{YY}$</th>
<th>$K_{ZZ}$</th>
<th>$K_{XY}$</th>
<th>$K_{XZ}$</th>
<th>$K_{YZ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-96.7</td>
<td>264.6</td>
<td>-167.9</td>
<td>-126.9</td>
<td>-28.8</td>
<td>51.9</td>
</tr>
<tr>
<td>2</td>
<td>-71.2</td>
<td>-115.8</td>
<td>187.0</td>
<td>0.0</td>
<td>-152.3</td>
<td>-50.0</td>
</tr>
<tr>
<td>3</td>
<td>-99.3</td>
<td>221.8</td>
<td>-122.5</td>
<td>90.3</td>
<td>15.1</td>
<td>62.2</td>
</tr>
<tr>
<td>4</td>
<td>-58.0</td>
<td>-128.0</td>
<td>186.0</td>
<td>0.0</td>
<td>136.2</td>
<td>-17.7</td>
</tr>
<tr>
<td>5</td>
<td>50.0</td>
<td>-96.5</td>
<td>46.0</td>
<td>75.7</td>
<td>-186.3</td>
<td>-84.3</td>
</tr>
</tbody>
</table>
TABLE VIII

Values of Electric Field Gradient Tensor Components in the System $z'\parallel a$ Multiplied by $K = 3eQ/2\hbar$ in kHz for the Five Deuteron Sites in Li$\text{N}_2\text{H}_5\text{SO}_4$.

<table>
<thead>
<tr>
<th>Site</th>
<th>$K_{x'x'}$</th>
<th>$K_{y'y'}$</th>
<th>$K_{z'z'}$</th>
<th>$K_{x'y'}$</th>
<th>$K_{x'z'}$</th>
<th>$K_{y'z'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>264.6</td>
<td>-167.9</td>
<td>-96.7</td>
<td>51.9</td>
<td>-126.9</td>
<td>-29.8</td>
</tr>
<tr>
<td>2</td>
<td>-115.8</td>
<td>187.0</td>
<td>-71.2</td>
<td>-50.0</td>
<td>0.0</td>
<td>-152.3</td>
</tr>
<tr>
<td>3</td>
<td>221.8</td>
<td>-122.5</td>
<td>-99.3</td>
<td>62.2</td>
<td>90.3</td>
<td>15.1</td>
</tr>
<tr>
<td>4</td>
<td>-128.0</td>
<td>186.0</td>
<td>-58</td>
<td>-17.7</td>
<td>0.0</td>
<td>136.2</td>
</tr>
<tr>
<td>5</td>
<td>-96.5</td>
<td>46.0</td>
<td>50.5</td>
<td>-84.3</td>
<td>75.7</td>
<td>-186.3</td>
</tr>
</tbody>
</table>
TABLE IX

Values of the Electric Field Gradient Tensor Components in the System $z'$ in the Plane of $a, b$ and $180^\circ$ from $z' || a$ Multiplied by $K = 3eQ/2h$ in kHz for the Deuterons of Sites 3, 4, and 5 Separately. Also Included Are the $D_3$ Average efg Tensor Values (Same Orientation).

<table>
<thead>
<tr>
<th>Site</th>
<th>$K_{x'x'}$</th>
<th>$K_{y'y'}$</th>
<th>$K_{z'z'}$</th>
<th>$K_{x'y'}$</th>
<th>$K_{x'z'}$</th>
<th>$K_{y'z'}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-122.5</td>
<td>381.7</td>
<td>-259.2</td>
<td>-54.5</td>
<td>33.6</td>
<td>-94.4</td>
</tr>
<tr>
<td>4</td>
<td>186</td>
<td>-120.9</td>
<td>-65.1</td>
<td>-58.9</td>
<td>124.3</td>
<td>20.6</td>
</tr>
<tr>
<td>5</td>
<td>46.0</td>
<td>-126.8</td>
<td>80.8</td>
<td>-22.7</td>
<td>-203.2</td>
<td>43.2</td>
</tr>
<tr>
<td>$ND_3$ (+72°)</td>
<td>36.7</td>
<td>28.5</td>
<td>-65.2</td>
<td>-16.3</td>
<td>7.0</td>
<td>10.7</td>
</tr>
<tr>
<td>$ND_3$ (-72°)</td>
<td>36.7</td>
<td>-36.5</td>
<td>0.2</td>
<td>9.1</td>
<td>-15.2</td>
<td>-10.7</td>
</tr>
</tbody>
</table>
The values of the components of the field gradient tensors, \( \phi_{ij} \), were obtained by transforming from the tensor expressed relative to the crystal system by a rotation about the appropriate crystal axis through an angle \( \theta \) to bring the z axis parallel to the field \( H_0 \). Table VII gives the components of the efg tensor in the crystal system for the bonds used in the analysis. The components of the efg tensor relative to a system in which \( z' \parallel a \) are given in Table VIII and the components of the efg tensor relative to a system in which the crystal is rotated about the c axis through the angle 72° from \( z' \parallel b \) are given in Table IX.

The transition probabilities were calculated on the assumption that the exchange causing relaxation is associated with rotation of the ND\(_3\) group or ND\(_2\) group, as opposed to exchange between neighboring N\(_2\)D\(_5\) groups. Using the values of \( P_1 \) and \( P_2 \) (see Table X) calculated for the a \( \parallel H_0 \) data, values of \( (S_0 - S(t)) \) can be plotted on semi-logarithmic paper against t. For values of \( S_0 - S(t) > 0.15 \) these plots are almost linear which explains the fact that the experimental response seems to depend on a single relaxation time. By fitting a straight line to these plots a single effective relaxation time is found. This effective relaxation time \( T_{1e} \) is calculated for both the ND\(_2\) and the ND\(_3\) groups with a \( \parallel H_0 \). The relaxation time for the ND\(_3\)
### TABLE X

Calculated Values of the $\Delta m = 1$ and $\Delta m = 2$ Transition Probabilities for the Cases of Interest

<table>
<thead>
<tr>
<th></th>
<th>$P_1$</th>
<th>$P_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ND_3(H_0 \parallel a)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega T_c &lt;&lt; 1$</td>
<td>$0.845 \times 10^{11} T_c / \text{sec}^2$</td>
<td>$2.02 \times 10^{11} T_c / \text{sec}^2$</td>
</tr>
<tr>
<td>$\omega T_c &gt;&gt; 1$</td>
<td>$\frac{0.845 \times 10^{11}}{\omega^2 T_c \text{ sec}^2}$</td>
<td>$\frac{0.505 \times 10^{11}}{\omega^2 T_c \text{ sec}^2}$</td>
</tr>
<tr>
<td>$ND_3(72^0 \text{ from } H_0 \parallel b \text{ about } c \text{ axis})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega T_c &lt;&lt; 1$</td>
<td>$0.993 \times 10^{11} T_c / \text{sec}^2$</td>
<td>$1.48 \times 10^{11} T_c / \text{sec}^2$</td>
</tr>
<tr>
<td>$ND_2(H_0 \parallel a)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega T_c &gt;&gt; 1$</td>
<td>$0.152 \times 10^{11} / \omega^2 T_c \text{ sec}^2$</td>
<td>$0.355 \times 10^{11} / \omega^2 T_c \text{ sec}^2$</td>
</tr>
</tbody>
</table>
A group with $z'$ in the ab plane $72^\circ$ from the b axis is obtained directly from $T_1 = (P_1 + 2P_2)^{-1}$. These calculated relaxation times all depend on $T_c$, the correlation time. The frequency $\omega = 2\pi \times 14.020$ MHz was employed for the entire experiment. The assumption is made that $T_c = T_0 \exp(E_a/kT)$ so that the calculated relaxation times depend on the parameters $E_a$ and $T_0$.

In the temperature region below 250 K (1/T > $4 \times 10^{-3}$/°K) a maximum in the $1/T_\text{r}$ curve is evident. The slopes of the curve in the regions above and below the peak are equal in magnitude, and depend through $T_c$ on the parameters $E_a$ and $T_0$. For temperature regions above and below the peak $T_1$ is proportional to $1/T_c$ and $\omega^2 T_c$ respectively. The assumption is made that at the peak the high temperature $T_1$ must equal the low temperature $T_1$. This equation contains only the variables $\omega$ and $T_c$. Since $\omega$ is known, the equation is solved for $T_c$ and it is found that $T_c = 1.02 \times 10^{-8}$ sec. By comparison the value obtained from the line width measurements at this temperature is $T_c = 4.3 \times 10^{-8}$ sec. The solid curve (Fig. 23) through this region is obtained by calculating $1/T_1 = \frac{5P_1 + P_2}{2}$ for $T_c$ in the region of $1.6 \times 10^{-8}$ sec. This expression was obtained from the initial slope of the return to equilibrium of the population following a 90° pulse. The value of $T_1$ calculated from the
The value of \( T_C \) at the intersection is \( T_1 = 7.6 \times 10^{-4} \) sec. The best fit to the data gives an activation energy \( E_a = 0.20 \pm 0.01 \text{eV} \) and \( T_0 = 1.6 \times 10^{-14} \) sec. The activation energy found by the line width technique is \( E_a = 0.19 \text{eV} \). By comparison \( E_a = 0.182 \pm 0.013 \text{eV} \) for the NH\(_3\) hindered rotation in LiH\(_2\)S\((12)\) and \( T_0 = 3 \times 10^{-14} \) sec for deuteron intrabond motion in KD\(_2\)PO\(_4\).\(^{(7)}\) A displacement in the best fit line occurs because of the difference in the values of \( T_1 \) depending on the orientation at which the measurement was made.

As the temperature increased, the value of \( 1/T_1 \) for the ND\(_3\) group begins to increase near \( 1/T = 2.80 \times 10^{-3}/\text{°K} \). This must be explained by some different mechanism. Three explanations are considered. First, it is possible that there is reorientation of the entire N\(_2\)D\(_5\) group. McClement, Pintar and Petch\(^{(13)}\) suggest that such a motion might cause the large reduction in second moment and the frequency dependent relaxation times observed for \( 1/T \times 10^3/T(\text{°K}) \) smaller than 3. However, the fact that the spectral lines due to the ND\(_3\) average are still observed at 2.2 and do not appear broadened, implies a \( T_C \) for such a motion larger than \( 10^{-5} \) sec. This large value for \( T_C \) leads to impossibly large differences in field gradient values (of the order \( 10^2 \) or \( 10^3 \) larger than those measured) in order to achieve the short
relaxation times observed. Thus tumbling of the hydrazine groups is not the mechanism for relaxation.

Secondly, diffusion may take place between ND$_3$ groups. If such a motion is assumed the ND$_3$ average field gradient values for neighboring hydrazine groups (Table IX efg axes oriented at $\pm 72^\circ$) can be used to determine $T_c$ from the $T_1$ values measured in this temperature region. Using $T_1 = 100$ milliseconds which is the value observed at

\[ \frac{1}{T} = 2/3 \times 10^{-3}/K \]

$T_c$ is calculated to be $1.6 \times 10^{-9}$ sec. This value of $T_c$ corresponds to $\omega T_c \ll 1$. However, the slope of the $1/T_1$ versus $1/T$ curve observed in this region corresponds to $\omega T_c \gg 1$ which makes diffusion between ND$_3$ groups an unacceptable explanation.

This leaves the possibility of jumping between ND$_2$ and ND$_3$ sites.

The $T_1$ measurements for the ND$_2$ group were carried out with the crystal oriented a $\parallel H_0$, making the relaxation behavior the same as that for the ND$_3$ group with a $\parallel H_0$. $P_1$ and $P_2$ are given in Table X and by best fitting Eq. (3.15) for these values of $P_1$ and $P_2$, the dependence of $T_1$ on $T_c$ is obtained. The $T_1$ values for the ND$_2$ group are 10 to 100 times shorter than those values predicted for the ND$_3$ relaxation time on the basis of jumping between ND$_3$ sites. It is reasonable that the jumping between ND$_2$ sites is the
primary relaxation mechanism for the deuterons of these sites. When a 90° pulse is applied to the ND$_3$ system, the ND$_2$ system stays approximately in equilibrium with the lattice since it has a much shorter $T_1$ than the ND$_3$ system. This means that the relaxation time measured for the ND$_3$ system is really a measure of the time for mixing between ND$_2$ and ND$_3$ populations.* Let this time be denoted $T_m$ and assume that $T_m = T_{mo} e^{E_a/kT}$. The best fit for the ND$_3$ relaxation then gives $E_a = -0.75 \pm 0.05$ eV and an unusually long infinite temperature mixing time, $T_{mo} = 1.3 \times 10^{-11}$ sec.

The effect of the mixing on the relaxation of the ND$_2$ group cannot be neglected. When the ND$_2$ system is subjected to a 90° pulse, the contribution due to mixing is $3/2$ the $1/T_1$ for the ND$_3$ site since it can be assumed that the ND$_3$ system stays nearly in equilibrium with the lattice during the short time that the ND$_2$ system relaxes. The factor $3/2$ is introduced because the $1/T_1$ for the ND$_3$ is proportional to the fraction of the number of deuterons occupying ND$_3$ sites exchanging with deuterons of ND$_2$ sites. There are only $2/3$ as many ND$_2$ sites as ND$_3$ sites so the jumping involves a fraction of the ND$_2$ sites $3/2$ larger than the fraction of ND$_3$ sites. The $1/T_1$ for ND$_2$ sites, since it is proportional to

*See Appendix B for discussion of equations governing this exchange process.
the fraction of \( ND_2 \) sites jumping, must be proportional to \( 3/2 \) the \( 1/T_1 \) for \( ND_3 \) sites. When this correction is made, the result is the dashed line in Fig. 23. The correlation time due to \( ND_2 \) hindered rotation has activation energy \( 0.50 \pm 0.02 \text{eV} \) and \( T_0 = 2.2 \times 10^{-14} \text{sec} \). By comparison the activation energy obtained by means of the line width study is \( 0.46 \text{eV} \).

**DISCUSSION.**

The measurements described in this chapter clearly indicate certain motions of the deuterons in the crystal. The deuterons of the \( ND_3 \) group undergo a hindered rotation. This rotation provides the principal mechanism for the relaxation of these deuterons up to about \( 65^\circ\text{C} \). The correlation time for this motion as indicated from the line width study is \( \sim 10^{-4} \text{sec} \) at \( 100^\circ\text{K} \).

The deuterons of the \( ND_2 \) group exchange at a lower rate. On the basis of the line width measurements, a correlation time of \( 10^{-5} \text{sec} \) is predicted for this exchange near room temperature. The merged lines observed due to the average over the \( ND_2 \) sites appear near \( 50^\circ\text{C} \) and the primary relaxation mechanism for these deuterons is provided by the exchange between \( ND_2 \) sites over the entire range studied, namely from \( T \approx 50^\circ\text{C} \) to \( T = 110^\circ\text{C} \).

Measurement of the dielectric constant reveals two
contributions to the relaxation mechanism. The low temperature contribution has an activation energy ~0.40eV comparable to that for the D2 exchange, while the high temperature contribution has an activation energy of about 0.70eV.

Jumping between the ND2 and ND3 sites explains the relaxation of ND3 site deuterons from 65°C to the upper limit of the temperature range available with the apparatus. The activation energy for this mechanism is 0.75 ± 0.05eV which is slightly larger than the quoted c axis dc conductivity activation energy of 0.65eV. However, the activation energy for the high temperature contribution to the dielectric relaxation of 0.70eV is in good agreement.

The agreement between the activation energies for the very large c axis dielectric constants and those for the ND2 exchange, and the ND2 to ND3 jumping indicates that the ND2 motion may be associated with the mechanism responsible for the dielectric relaxation.

As is indicated in Fig. 1 there are n glides, b glides and twofold rotation axes in the crystal cell. Because of this symmetry of the crystal, reflection through the ab plane of a unit cell gives rise to a deuteron splitting spectrum identical to the spectrum observed for the unreflected cell. This coupled with the absence of any
positive indication in either the low temperature spectrum or the high temperature spectrum of a doubling of spectral lines is consistent with the idea that domain reversal takes place by way of reflection through the ab plane.

Although the deuteron spectrum above -85°C shows change, which is possibly due to structural change in the crystal, no definite conclusions can be made as to the exact nature of the change. Certainly no indication of a ferroelectric transition is obtained below 190°C. This is in agreement with the absence of an anomaly in the dielectric constant below 200°C, which substantiates earlier claims (10) that no ferroelectric transition takes place below the decomposition temperature of the crystal.
CHAPTER IV EXPERIMENTAL

CRYSTAL PREPARATION.

Single crystals of LiN_{2}H_{5}SO_{4} were prepared by dissolving stoichiometric amounts of Li_{2}CO_{3} (reagent grade) and (NH_{2})_{2}H_{2}SO_{4} (reagent grade) in water, and crystallizing by slow evaporation. Large (2.95cm x 3.05cm x 5.6cm, 34g.) single crystals with well developed (100), (110) and (101) faces can be grown by this technique. In order to obtain deuterated samples, the crystals of LiN_{2}H_{5}SO_{4} obtained as described above were dissolved in 90% D_{2}O and recrystallized. An estimate of the percent of deuteration of these crystals was made by comparing proton signal strengths from two samples of equal size. The results indicated that the crystal was about 50% deuterated. A second recrystallization from 99% D_{2}O was then carried out. The crystallizing dish was placed in a desiccator during this process in order to minimize water vapor exchange with the atmosphere.

NMR SPECTRA.

A Robinson(32) circuit employing frequency modulation between 900 and 1500 Hz and operating at 14 MHz was used to obtain most of the NMR spectra. A solid state modification of this circuit(33) was used to obtain the room temperature data.

The permanent magnetic field for the experiment was
provided by a 15" Varian electromagnet with Model V-FR-2703 Fieldial control. The crystal was oriented relative to the permanent field $H_0$ by visually aligning it with a crystal axis parallel to the spectrometer tube. The spectrometer tube was fixed perpendicular to the circular spectrometer base plate, which was calibrated in degrees. The spectrometer then rested on its base in a circular holder in such a fashion that rotating the spectrometer in its holder rotated the tube and hence the crystal about the crystal axis perpendicular to the field. The rotation angle was read from the circular base plate.

The spectrum corresponding to a particular crystal orientation was typically obtained in the following fashion. The field dial was set so that the sweep center coincided with the center of the NMR spectrum and then the magnetic field was swept over the range including the spectrum. The sweep range varied from 50 gauss to 500 gauss depending on crystal orientation and temperature. Sweep times between 1 and 25 minutes were used.

The room temperature spectrum and part of the $77^\circ$K spectrum were obtained using a Princeton Applied Research (P.A.R.) Model JB-4 lock-in amplifier as the modulation source for the spectrometer, and signal detector and amplifier. All the remaining data was obtained using a
P.A.R. Model HR-8 lock-in amplifier. The output of the lock-in was ordinarily fed directly to either a Bristol time base chart recorder (Fig. 4 shows typical spectra) or a Moseley 7000 AR X-Y recorder (Fig. 16 shows typical spectra). The X drive for the X-Y plotter was provided by an output from the Fieldial magnet sweep control. The operating frequency of the spectrometer was monitored by a Hewlett Packard 5245L electronic counter with 5261A preamplifier.

Poor signal to noise ratio made necessary the employment of a signal averaging technique in order to obtain the spectra for certain orientations. The output of the lock-in detector was fed to a Vidar Model 240 voltage-to-frequency converter and the output of the converter was then stored in a Technical Measurement Corporation Model 401D 400 channel amplifier. The magnetic field sweep was coordinated with the storage rate of the multichannel analyzer. The accumulated storage of from 3 to 10 sweeps was then called out of the multi-channel analyzer and recorded in a form suitable for analysis. A block diagram of the experiment is shown in Fig. 24.

Temperatures for this experiment were held within ±5°C for obtaining spectra, and within ±1°C for the line width study. The 77°K spectrum was obtained by submerging, in a
Fig. 24. Block Diagram of NMR Spectrometer.
Dewár of liquid air, the sample and sample coil which were sealed in a brass can. The temperature at the boiling point of liquid air at Bozeman is 77.3°K. The 193°K spectrum was obtained by submerging the sample sealed in a brass can in a Dewar of methanol. The temperature of the methanol was controlled by the addition of liquid air. A chromel-alumel thermocouple was used to measure the temperature of the bath. Some of the measurements taken at 65° and 95°C were obtained using as a bath silicone oil heated with a resistor. The line broadening of the ND₂ group was studied in this same fashion. The remainder of the measurements at elevated temperature were made by means of an electric heater in good thermal contact with a brass can surrounding the sample.* A stainless steel insulating tube was placed around the heating coil, thermal connector and sample to provide thermal isolation for the system. The temperature control employed to obtain ±1° tolerance for the line broadening data at low temperature was effected by means of a spectrometer tube built as an integral part of a liquid air reservoir.* The neck separating the sample coil from the reservoir was wound with a heating element and control is exercised by means of

*The two temperature control devices are pictured in detail in reference 34.
the current passed through the heating element.

CONDUCTIVITY AND DIELECTRIC CONSTANT.

Samples suitable for both conductivity and dielectric constant measurements were obtained by cutting small wafer-shaped sections from large single crystals with a string saw. Care was taken to guarantee that the normals to the large surfaces or faces of these wafers were parallel to a crystal axis. These faces were then polished with a damp paper and contacts were painted on them. One contact was a round dot with average area of 4x10^{-2} cm^2. A guard ring was then painted around the circular contact. The average thickness for the samples was about 0.15 cm.

A block diagram of the conductivity experiment is shown in Fig. 25. The conductivity is

\[ \sigma = \frac{1}{\rho} = \frac{t}{A} \times \frac{1}{R_c} , \]

where \( t \) = crystal thickness, \( A \) is the area of the circular contact, and \( R_c \) is the resistance of the crystal. (The crystal equivalent circuit is shown in Fig. 26). The current through the crystal is the sum of the current through \( R_c \) and \( R_s \). \( R_g \) represents the resistance through the crystal to the guard ring, including the surface between the ring and the contact on the opposite crystal.
Fig. 25. Block Diagram of Conductivity Experiment
-81-

face. $R_s$ is the resistance between guard ring and the center contact on the same face, and $R_c$ is the crystal resistance.

Fig. 26. Crystal Equivalent Circuit

If $R$ is made small compared to $R_c$ and $R_s$, then the current through $R_s$ is negligible compared to that through $R_c$, so the current through the electrometer resistance $R$ is approximately the current through $R_c$ and since $IR << IR_c$ the voltage $V_0$ is dropped almost entirely across $R_c$. Thus $R_c = \frac{V_0}{I}$ to a good approximation, where $V_0$ is the applied voltage and $I$ is the current measured through the electrometer. For voltages between 10 and 300 volts a Dressen Barnes 5-300F regulated power supply was used to supply $V_0$. The voltage was measured with a J. Fluke Model
881 differential voltmeter. Below 10 volts the differential voltmeter was used as the source of $V_0$. Typical values for the crystal resistance range between $10^7$ and $10^{15}$ ohms for the assortment of samples and temperatures studied. Electrometer resistance was held at least 100 times smaller than $R_c$. In order to accomplish this, a General Radio Model 1230A electrometer was used as a Keithley Model 148 nanovoltmeter.

Elevated temperatures were obtained by placing the sample probe within a leak-proof container and submerging the assembly in a bath of mineral oil. The bath temperature was controlled by controlling the current through a resistor in the bath. Lower temperatures were obtained by using methanol as a bath and adding liquid air in small amounts. The temperature was measured with a chromel-alumel thermocouple, which was used to provide the x axis drive voltage for the Moseley 7000 AR X-Y plotter. The output of the electrometer was fed into the y axis input of the plotter. This allowed a continuous measurement of the crystal current vs temperature. The voltage applied to the sample was reversed periodically in order to minimize build-up of high resistance layers adjacent to the electrodes (electrode "polarization"). Upon reversing the voltage,
large transient current was observed. The average current indicated after the decay of the transient was taken to be representative of the crystal conductivity.

The ac dielectric constant was measured with a bridge circuit. A diagram of the circuit is shown in Fig. 27. The crystal holder is pictured in Fig. 28.* A Tektronix 541A oscilloscope with a Type IA2 dual preamp in the subtract mode, which provides for superposition of the signals in the two channels of the preamp, was used to detect the balanced bridge condition. For measurements of the a axis dielectric constant the P.A.R. Model HR8 lock-in detector with the preamplifier in the difference mode was used. With the bridge balanced the capacitance and resistance of the sample are in the same ratios to $C_v$ and $R_v$ as $C_1$ and $R_1$ are to $C_2$ and $R_2$. The following equations are then used to calculate the real and imaginary parts of the dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$

$$
\varepsilon' = \frac{tC_c}{\varepsilon_0A} \\
\varepsilon'' = \frac{t}{\varepsilon_0\omega AR_c}
$$

Here $C_c$, $R_c$, and $t$ are the sample capacitance, resistance and thickness respectively, $A$ is the area of contact, and

*The crystal holder was designed and constructed by Prof. V. H. Schmidt.
Fig. 27. Diagram of Dielectric Constant Measurement Circuit.
Fig. 28. Sample Probe Employed for the Dielectric Constant Measurement.
\( \omega \) the angular frequency of the ac voltage at which the measurement is made.

The temperature of the crystal was controlled by placing the sample holder in its protective brass container in a bath of fine sand. Temperatures above room temperature were obtained by passing a current through a resistor buried in the sand bath. To lower the temperature, the bath was cooled by adding small quantities of liquid air. The temperature was measured with a chromel-alumel thermocouple.

RELACTION TIME.

The spin-lattice relaxation time measurements were made with a double 90° pulse sequence. The initial trigger was supplied by a pulse generator supplying single pulses at 1.3 sec to 5 min intervals. The trigger was fed to a Tektronix Type 162 waveform generator, which produces a sawtooth of variable length as well as a pulse. The pulse and sawtooth were fed separately to two Tektronix Model 163 pulse generators to allow the 163 triggered by the sawtooth to fire at a time after the 163 triggered from the pulse. This time was controlled by changing the point along the sawtooth at which the voltage had risen to a value sufficient to trigger the pulse generator. Pulse lengths and separation were measured with a Hewlett Packard 5245-L
electronic counter with 5262A time interval unit and an H.P. 5321A time interval unit. The outputs from the pulse generators were fed to a pulse amplifier and then to an rf gating circuit which derives rf input from a crystal controlled 14.020 MHz oscillator. The output of the rf gate drives an rf pulse transmitter.* The output of the pulse transmitter is fed to a crossed coil pulse head. The nuclear decay signal is picked up in the sample holder and fed to a preamplifier and then to a pulse receiver. The signal output of the receiver was measured with a boxcar integrator, the output of which is measured by a Minneapolis Honeywell potentiometer, Model 2730. A block diagram of the apparatus is pictured in Fig. 29.

A typical measurement is obtained by subjecting the sample to two 90° pulses separated by a time t. The nuclear signal is measured during the tail following the second pulse by feeding the output of the pulse receiver during a brief period of the tail into the boxcar integrator. By repeating this procedure for many pulse sequences, noise is averaged and the output of the boxcar is measured with the potentiometer. The time t separating

*The pulse apparatus was constructed by Robert Parker and Fred J. Blankenburg. The basic design is after Clark et al. (35,36)
Fig. 29. Block Diagram of Pulse Apparatus
A - Trigger Pulse Generator
B - Tektronix Model 162 Waveform Generator
C - Tektronix Model 163 Pulse Generator
D - Tektronix Model 163 Pulse Generator
E - Pulse Amplifier
F - Radio Frequency Gate
G - Crystal Controlled Oscillator
H - Radio Frequency Pulse Transmitter
I - Radio Frequency Preamplifier
J - Pulse Amplifier
K - Box Car Integrator
L - Potentiometer

Key for Fig. 29
the two pulses is changed and the entire procedure is repeated. The slope of a semilog plot of signal voltage versus t makes possible the calculation of the spin-lattice relaxation time $T_1$.

Temperature control is achieved by passing hot or cold air into the pulse head in such a fashion that the air is directed uniformly over the crystal. Cold air is provided by boil-off from a container of liquid air. Heated air is obtained by passing air from the Physics Building compressed air system through a regulator, then through a tube containing an electric heating element and finally into a pulse head. The temperature was measured with a chromel-alumel thermocouple attached to the crystal. Temperature variation for the measurements above room temperature was ±1°C and below room temperature ±1.5°C.
APPENDIX A

Nuclei of spin $I > 1$ may possess an electric quadrupole moment.* If such a nucleus is placed at a site of non-vanishing electric field gradient (efg), and interaction between the nuclear quadrupole moment and the efg may be observed. The Hamiltonian of such an interaction, $H_Q$, is given by the tensor product of the nuclear quadrupole moment tensor with the efg tensor. Transitions between the energy states of the system can be induced by coupling the magnetic component of a resonant radio frequency field ($E = h\nu$) with the magnetic moment of the nucleus. In this fashion it is possible to measure the interaction energy characterized by $H_Q$.

Three important cases are distinguished with regard to this problem. The first case, that termed pure nuclear quadrupole resonance, is outlined above. The second case, called the weak field or Zeeman case, consists of subjecting the system of nuclei at sites of nonzero efg, to a weak permanent magnetic field $H_0$ (~10 gauss). The Hamiltonian for the system is then $H_{\text{tot}} = H_Q + H_{\text{mag}}$, where the magnetic interaction is treated as a perturbation on the quadrupolar interaction energy. The third case consists of subjecting

*General discussion of the topic of this appendix is found in references 37 and 38.
a system of nuclei wherein the quadrupolar interaction is relatively small, to a strong magnetic field ($\sim 10^4$ gauss). The Hamiltonian is then $H_{\text{tot}} = H_{\text{mag}} + H_Q$ with $H_Q$ the perturbation.*

In the present work the problem was the determination of the efg tensor at the hydrogen sites. In order to do this, deuterons ($Q = 2.77 \times 10^{-24}$ cm$^2$) were substituted for protons ($Q=0$). The experiment falls in the category of case 3. The calculation of the energies proceeds by choosing a representation in which $I^2$ and $I_z$ are simultaneously diagonal. The basis states are denoted, $|I,m,n\rangle$, where

$\begin{align*}
I^2|I,m,n\rangle &= I(I+1)|I,m,n\rangle, \\
I_z|I,m,n\rangle &= m|I,m,n\rangle.
\end{align*}$

The energy to zeroth order is the magnetic interaction energy

$E_0 = (I,m| - \gamma H_0 I_z|I,m)$

(A.1)

$\gamma H_0 m$

where $H_0$ is the permanent magnetic field directed along the $z$ axis, $\gamma$ is the gyromagnetic ratio, $I_z$ is the $z$ component of the nuclear angular momentum operator, and $m$ is the magnetic quantum number. The perturbation is

*This case is considered by Volkoff(39) and the experiment is described in detail in the work of Volkoff, Petch and Smellie.(40)
\[ H_Q = \frac{eQ}{2I(2I-1)} \left\{ (3I_z^2 - I^2)(\nu E)_o + \frac{\sqrt{6}}{2}(I_z I_+ + I_+ I_z)(\nu E)_{-1} \right. \]
\[ + \left. \frac{\sqrt{6}}{2}(I_z I_- + I_- I_z)(\nu E)_{+1} + \frac{\sqrt{6}}{2}I^2(\nu E)_{-2} + \frac{\sqrt{6}}{2}I^2(\nu E)_{+2} \right\}. \]

\( e \) is the electron charge, \( Q \) the nuclear quadrupole moment and \( I \) is the nuclear angular momentum. The raising and lowering operators are defined \( I_\pm = (I_x \pm iI_y) \) and the components of the efg tensor (with the \( z \) axis established by the magnetic field \( H_0 \)) are given by

\[ (\nu E)_o = \frac{1}{2} \phi_{zz} \]
\[ (\nu E)_{\pm1} = \pm \frac{1}{\sqrt{6}} (\phi_{zx} \pm i\phi_{yz}) \]
\[ (\nu E)_{\pm2} = \frac{1}{2\sqrt{6}} (\phi_{xx} - \phi_{yy} \pm 2i\phi_{xy}) . \]

The first order correction is

\[ E_1 = \frac{eQ}{2I(2I-1)} \left[ 3m^2 - I(I + 1) \right] (\nu E)_o . \]

The second order correction is

\[ E_2 = \left( \frac{eQ}{2I(2I-1)} \right)^2 \left[ \frac{3}{g\beta H_0} \left( m \left[ 4I(I + 1) - 1 - 8m^2 \right] \right) \right] \left| (\nu E)_{\pm1} \right|^2 \]
\[ - \frac{3}{g\beta H_0} \left( m \left[ 2I(I + 1) - 2m^2 - 1 \right] \right) \left| (\nu E)_{\pm2} \right|^2 . \]
In general $|\nabla E_\mu|^2 (\mu = \pm 1, 2)$ can be expressed in units of $e^2 q^2 |\nabla E_\mu|^2$ relative to $z$ $\Gamma H_0$ with $x, y$ arbitrary. Then

$$|\nabla E_\mu|^2 = e^2 q^2 |\nabla E_\mu|^2$$  \hspace{1cm} \text{(A.8)}

and setting $\frac{e^2 q q}{\hbar} = k$ (coupling constant) and $\frac{g \beta H_0}{\hbar} = h \nu_L$ ($\nu_L$, the Larmor frequency of the nucleus)

$$E_1 = \frac{\hbar K}{2I(I+1)} \left[3m^2 - I(I + 1)\right] (\nu E)_0$$  \hspace{1cm} \text{(A.9)}

and

$$E_2 = \frac{3h}{2I(I+1)^2} \frac{K^2}{\nu_L} \left[3(m \left[4I(I + 1) - 1 - 8m^2\right]) |(\nu E)_{\pm 1}|^2ight] - 3(m \left[2I(I + 1) - 2m^2 - 1\right]) |(\nu E)_{\pm 2}|^2.$$  \hspace{1cm} \text{(A.10)}

It can be seen that $K/\nu_L$ measures the magnitude of $E_2$ relative to $E_1$. The maximum value for the coupling constant is about 200 kHz. The Larmor frequency is 14 MHz. This makes $\frac{K}{\nu_L} = 2 \times 10^5 \frac{1.4 \times 10^7}{1.4 \times 10^7}$ and $E_2$ down some two orders of magnitude from first order effects. The shift in the center of the pattern resulting from the second order effect would then be of the same magnitude as the line widths observed. This is about the same size as the estimated error in the experiment, hence the second order effect is not studied.

It can be seen that the first order correction depends on

\*Z\* denotes the axis of the largest component of the efg tensor expressed in diagonal form.
the nuclear spin \( I \), the nuclear quadrupole moment \( Q \), and
the quantity \( (\nabla E)_o = \frac{1}{2} \phi_{zz} \) where \( \phi_{zz} \) is the second derivative
of the electrostatic potential at the nuclear site, with \( z \) parallel to \( H_0 \).

For deuterons the energy is given by

\[
E = -\gamma H_0 m + \frac{eQ}{2} \left( 3m^2 - 2 \right) \phi_{zz}
\]

(A.11)

The magnetic levels of the deuteron are shifted by the
quadrupole interaction, causing the single absorption line
at \( \gamma H_0 \) to split into two lines spaced equally on both sides
of the unperturbed line, as pictured in Fig. 30. These
lines are separated by a frequency \( 3eQ/h(\nabla E_0) \).

\[
\begin{array}{c}
\text{a) Zeeman Levels and Transition Frequency} \\
m=-1 \quad \gamma H_0 \\
\text{b) Zeeman Levels Shifted by 1st Order Quadrupole} \\
\text{Perturbation and Corresponding Transition Frequencies.}
\end{array}
\]
Changing the orientation of the sample relative to the constant field $H_0$, changes the component of the efg tensor along $H_0$. The result is that the splitting observed between the spectral lines changes. Because the efg tensor is symmetric ($\nabla \times E = 0$) and traceless ($\nabla \cdot E = 0$) it has only five independent components. The tensor can be put into the form

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

(A.12)

where $eq$ is the largest and $-eq(1-\eta)/2$ the smallest component, making $|\phi_x'x' - \phi_y'y'| \phi_z'z'| = \eta$ lie in the range $0 \leq \eta \leq 1$. The values of $\eta$, $eq$, and three independent direction cosines specifying the orientation of the diagonal tensor relative to the crystal axes constitute five independent quantities.

A transformation can be carried out between the crystal and laboratory systems which relates the efg tensor to the system fixed in the crystal, through Eq. (2.1). The $A$, $B$ and $C$ of Eq. (2.1) are related to the components of the efg tensor in the crystal system as follows:

$$
A_i = \frac{3eq}{2h} (\phi_{jj} + \phi_{kk}) = -\frac{3eq}{2h} \phi_{ii}
$$

(A.13)
As was discussed in Chapter I, the experimental curves of splitting frequency versus angle for rotation about the three crystal axes determine values for the A, B and C from which are found the components of the efg tensor in the crystal system. This tensor is then diagonalized and the values of the coupling constant, asymmetry parameter and the orientation of the efg tensor principal axis system in the crystal are obtained.

\[ B_i = \frac{3eQ}{2\hbar} (\phi_{jj} - \phi_{kk}) \]  
\[ C_i = -\frac{3eQ}{2\hbar} \delta_{jk}; i, j, k = x, y, z \]
APPENDIX B

The deuteron system is a three level system so that relaxation processes may take place by way of $\Delta m = 1(P_1)$ or $\Delta m = 2(P_2)$ transitions. In order to calculate the probability of a transition between levels of the system, it is assumed that the mechanism responsible for the transition is the fluctuation in the nuclear quadrupole interaction due to deuteron jumping between sites of different electric field gradient. The calculation proceeds\(^{(9)}\) by taking as the probability per unit time of a transition between states $k$ and $m$

$$P_{mk} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} G_{mk}(T)e^{-i(m-k)T}dT \quad (B.1)$$

where the correlation function is defined

$$G_{mk}(T) = \langle m|H_Q(t)|k\rangle\langle k|H_Q(t+T)|m\rangle \quad (B.2)$$

the bar denoting an ensemble average over all values of $(m|H_Q(t)|k)$. The value of $G_{mk}(T)$ must be determined for two cases, exchange between two sites ($ND_2$ group) and exchange among three sites ($ND_3$ group). Having determined the values for $G_{mk}(T)$ for these two cases, it is then possible to calculate $P_{mk}$ for the two cases. The relaxation times are then calculated from a knowledge of the population distributions immediately following a $90^\circ$ pulse. Substitution of the values for $P_1$ and $P_2$ calculated
above yield expressions for the relaxation times depending only on the correlation time $T_c$, and the Larmor frequency of the nucleus.

Consider first the calculation of $G_{mk}$ for the case of jumping between two sites. Denote the sites as site 1 and site 2 corresponding to the deuteron positions indicated in Chapter II. Let $\xi_m = E_m$ and $\xi_k = E_k$ so that

$$(m - k) = (E_m - E_k) = \omega.$$ Assume that exchange takes place as follows. Let there be $n$ nuclei equally distributed between sites 1 and 2, and consider nuclei that at $T = 0$

a) occupy site 1 or b) occupy site 2. The element of the ensemble average corresponding to a is then

$$\frac{F_1}{2} \left[ P_1(T)F_1 + P_2(T)F_2 \right]$$

where $F_1(i = 1, 2)$ denotes that part of the Hamiltonian representative of the environment of site 1 which differs from site 2, so that as the nuclei exchange from site 1 to site 2 the interaction energy changes. For the case under consideration, $F_1$ represents the factor in the matrix element of $H_Q$ containing the efg components. $P_i(T)$ is the probability that at time $T$, the nucleus will be found at site 1. The remaining element of the ensemble average is

$$\frac{F_2}{2} \left[ P_1(T)F_1 + P_2(T)F_2 \right]$$
corresponding to b. Then

$$F(0)F(T) = \frac{F_1}{2} \left[ P_1(T)F_1 + P_2(T)F_2 \right] + \frac{F_2}{2} \left[ P_1(T)F_1 + P_2(T)F_2 \right].$$

To determine $P_1(T)$ and $P_2(T)$, choose an ensemble with $n_1$ nuclei in site 1 and $n_2$ nuclei in site 2. Let $n_1 + n_2 = n$ and denote the probability of rotation through $+180^\circ$ between sites 1 and 2, $P_{r+}$ so that $P_{r+} = P_{r-} = \frac{P_r}{2}$, $P_r$ being probability of exchange due to $+180^\circ$ rotation. The equations describing the populations are, denoting $\frac{d}{dt}$ by $\dot{}$,

$$\dot{n}_1 = -P_r n_1 + P_r n_2 = -n_2$$

$$\dot{n}_2 = -P_r n_2 + P_r n_1$$

which are satisfied by $n_1 = \frac{n}{2} + \frac{n_2}{2} e^{-2P_r T}$ and $n_2 = \frac{n}{2} - \frac{n_2}{2} e^{-2P_r T}$; then $P_1(T) = \frac{n_1}{n} = \frac{1}{2} (1+e^{-2P_r T})$ and $P_2(T) = \frac{n_2}{n} = \frac{1}{2} (1-e^{-2P_r T})$ making

$$F(0)F(T) = \frac{F_1}{2} \left[ \frac{1}{2}(1+e^{-2P_r T})F_1 + \frac{1}{2}(1-e^{-2P_r T})F_2 \right]$$

$$+ \frac{F_2}{2} \left[ \frac{1}{2}(1-e^{-2P_r T})F_1 + \frac{1}{2}(1+e^{-2P_r T})F_2 \right]$$

$$= \text{constant} + \frac{F_1}{4} \left[ e^{-2P_r T}F_1 - e^{-2P_r T}F_2 \right]$$

$$+ \frac{F_2}{4} \left[ -e^{-2P_r T}F_1 + e^{-2P_r T}F_2 \right].$$

(B.5)
The constant term does not contribute to the relaxation and is dropped. This leaves

\[ F(o)F(T) = \frac{1}{4} (F_1 - F_2)^2 e^{-T/T_c} \]

where \( 2P_r = 1/T_c \).

Then for the \( \Delta m = 1 \) transition,

\[ G_{\Delta 1}(T) = \left[ \frac{e^{0}}{4I(2I-1)} \right] (2m \pm 1) \left[ (I \pm m)(I \pm m + 1) \right] \frac{i_b}{2} \]

\[ \frac{1}{4}(F_1 - F_2)^2 e^{-T/T_c} \] (B.6)

Here \( F_i = \frac{1}{2}(\phi_{xx_i} - \phi_{yy_i}) \pm i\phi_{xy_i}, \) \((i = 1,2)\) denoting sites 1 or 2. Specializing to \( I = 1 \) makes

\[ G_{\Delta 1}(T) = \frac{e^{2Q^2}}{32} (F_1 - F_2)^2 e^{-T/T_c} \] (B.7)

and

\[ P_1 = \frac{4\pi^2}{h^2} \int_{-\infty}^{\infty} \frac{e^{2Q^2}}{32} (F_1^2 - F_2^2) e^{-T/T_c - i\omega T} dT \]

\[ = \frac{\pi^2 e^{2Q^2}}{4h^2} \left[ (\Delta\phi_{xz})^2 + (\Delta\phi_{yz})^2 \right] \frac{T_c}{1 + \omega^2T_c^2} \] (B.8)

where \( \Delta\phi_{ij} \) means \( \phi_{ij}(\text{site 2}) - \phi_{ij}(\text{site 1}) \). For the \( \Delta m = 2 \) transition

\[ G_{\Delta 2}(T) = \frac{e^{2Q^2}}{4} (F_1 - F_2)^2 e^{-T/T_c} \] (B.9)

which gives for the transition probability

\[ P_2 = \frac{4\pi^2}{h^2} \int_{-\infty}^{\infty} \frac{e^{2Q^2}}{4} (F_1^2 - F_2^2) e^{-\frac{T}{T_c} - i2\omega T} dT \] (B.10)
The same arguments are then applied to the case of jumping among sites 1, 2 and 3. Transition probabilities obtained for exchange among the sites 1, 2 and 3 are

\[ P_1 = \frac{\pi^2 e^2 q^2}{9\hbar^2} \left[ (\Delta_{12}\phi_{xz})^2 + (\Delta_{13}\phi_{xz})^2 + (\Delta_{23}\phi_{xz})^2 \right. \]
\[ + (\Delta_{12}\phi_{xy})^2 + (\Delta_{13}\phi_{yz})^2 + (\Delta_{23}\phi_{yz})^2 \left. \right] \frac{T_c}{1 + \omega^2 T_c^2} \]  
(B.12)

and

\[ P_2 = \frac{\pi^2 e^2 q^2}{18\hbar^2} \left[ (\Delta_{12}\phi_{xx} - \phi_{yy})^2 + (\Delta_{13}\phi_{xx} - \phi_{yy})^2 \right. \]
\[ + (\Delta_{23}\phi_{xx} - \phi_{yy})^2 \left. \right] + 4 \left[ (\Delta_{12}\phi_{xy})^2 + (\Delta_{13}\phi_{xy})^2 \right. \]
\[ + (\Delta_{23}\phi_{xy})^2 \left. \right] \frac{T_c}{1 + \omega^2 T_c^2} \]  
(B.13)

where \( \Delta_{ab}\phi_{ij} = (\phi_{ij})_a - (\phi_{ij})_b \), a and b denoting site numbers.

These expressions for the \( \Delta m = 1,2 \) transition probabilities will now be used to calculate the relaxation times for the cases under consideration. The first of these is saturation of the two lines at a crossing point. The three levels are populated at equilibrium with \( N_{-1}, N_0 \) and
$N_{+1}$ nuclei in the $m = -1$, $m = 0$ and $m = +1$ levels respectively. Because the levels are almost equally spaced, one can to good approximation let $N_0 - N_{-1} = n_0$ and $N_{+1} - N_0 = n_0$. Let $n_1$, $n_2$ and $n_3$ denote variations from equilibrium of the populations of levels $m = -1, 0$ and +1 respectively. These populations then may be pictured as in Fig. 30, where $n_1 = -n_2 - n_3$. The signal observed at time $t$ is proportional to $2n_s$, where $n_s = n_3 - n_2 + n_0$.

$$n_3 = -n_3 p_1 - n_3 p_2 + n_2 p_1 - (n_3 + n_2) p_2$$

$$= -n_2 (p_1 + 2p_2) + n_2 (p_1 - p_2) \quad (B.14)$$

but $n_2 = 0$ and $n_2 = 0$ so that $n_3 + (p_1 + 2p_2) n_3 = 0$, which has the solution $n_3 = -n_0 e^{-(p_1 + 2p_2)t}$, and by symmetry

$$n_1 = n_0 e^{-(p_1 + 2p_2)t}.$$ Then $n_s = n_0 - n_0 e^{-(p_1 + 2p_2)t}$

$$= n_0 (1 - e^{-t/T_1}) \text{ where } 1/T_1 = p_1 + 2p_2 \text{ and thus }$$

$$S_0 - S(t) = S_0 e^{-t/T_1} \text{ where } S_0 \text{ is equilibrium signal height.}$$

Now for the case wherein only one of the lines is saturated, the populations are disturbed as pictured in Fig. 31. The signal at time $t$ is proportional to $n_s$ and

$$n_s = n_2 - (-n_0 + n_1).$$

$$n_1 = -n_1 (p_1 + 2p_2) + n_2 (p_1 - p_2) \quad (B.15)$$

and

$$n_2 = -2p_1 n_2 + p_1 n_1 - p_1 (n_2 + n_1) = -3p_1 n_2. \quad (B.16)$$
Fig. 31. Relative Populations of Nuclear Levels as a Function of Time for Symmetric Saturation. At $t = 0$, a $90^\circ$ Pulse Saturates the System.

Fig. 32. Relative Populations of Nuclear Levels as a Function of Time for Saturation of Single Line. At $t = 0$ $90^\circ$ Pulse Saturates $m = (0\leftrightarrow-1)$ Transition.
These equations are satisfied by \( n_2 = \frac{-n_0 e^{-3P_1 t}}{2} \) and

\[
n_1 = \frac{n_0 e^{-3P_1 t}}{4} + \frac{n_0 e^{-(P_1+2P_2) t}}{4}
\]

making

\[
n_s = n_0 \left( 1 - \frac{3}{4} e^{-3P_1 t} - \frac{1}{4} e^{-(P_1+2P_2) t} \right)
\]

and

\[
S_0 - S(t) = \frac{1}{4} \left( 3e^{-3P_1 t} + e^{-(P_1+2P_2) t} \right) S_0.
\]

Finally the mechanism proposed for relaxing the \( ND_3 \) deuterons by exchange to \( ND_2 \) sites is considered.

The population of the \( m = -1, 0, +1 \) levels are denoted as pictured in Fig. 32. Since there are three \( ND_3 \) sites to every two \( ND_2 \) sites the populations are multiplied by the appropriate numerical factors. The experiment is carried out at a crossing, guaranteeing symmetric saturation of the \( ND_3 \) system. This makes \( n_{32} = 0 \) for all \( t \), \( n_{23} = -n_{21} \), and \( n_{33} = -n_{31} \). Then the rate equation governing \( n_{31} \) is given by

\[
n_{31} = -p(n_{31} - n_{21})
\]

where \( p \) denotes the probability that a deuteron at an \( ND_3 \) site jumps to an \( ND_2 \) site.

The rate equation for the corresponding level of deuterons of the \( ND_2 \) group is

\[
n_{21} = -(P_1+2P_2+\frac{3}{2}p)n_{21} + \frac{3}{2}pn_{31}.
\]
P_1 + 2P_2 is identified as 1/T_1 governing relaxation for the case of symmetric saturation of the three level deuteron system and will be denoted P.

By substitution, the following differential equation for n_{31} is obtained

$\dot{n}_{31} + \frac{5}{2}Pn_{31} + Pn_{31} + Ppn_{31} = 0$.  \hspace{1cm} (B.19)

No confusion will be encountered by dropping the subscript 1 since the ND_3 as well as the ND_2 rates are symmetric in levels 1 and 3.

\[ \begin{align*}
3n_0 + 3n_{33} \\
3n_{32} \\
3n_0 + 3n_{31} \\
2n_0 + 2n_{23} \\
2n_{22} \\
-2n_0 + 2n_{21}
\end{align*} \]

**Fig. 33.** Relative Populations of Nuclear Levels as a Function of Time for Symmetric Saturation of the ND_3 System, Indicating Coupling with ND_2 System.
Assuming the solution $n_3 = n_a e^{c_1 t} + n_b e^{c_2 t}$, with $n_a + n_b = n_0$, and that $P \gg p$, a solution $n_3 = n_a e^{-pt} + n_b e^{-pt}$ is obtained.

Now since $P \gg p$, i.e., the jumping between ND$_3$ and ND$_2$ sites occurs much more slowly than the relaxation of deuterons of the ND$_2$ group, the relaxation rate is limited by $p$, because $n_a = 0$ and $n_b = n_0$, with the result that $n_3 = n_0 e^{-pt}$.

If the ND$_2$ system is saturated, the relaxation is due primarily to jumping between the two ND$_2$ sites. Since $n_{13} = 0$ it follows from Eq. (B.18) that the time constant for the return to equilibrium is $(P_1 + 2P_2) + \frac{3}{2}p$. However, the experiment for the ND$_2$ group is not carried out at a crossing, so the $T_1$ due to ND$_2$ hindered rotation is governed by Eq. (3.15), rather than $(P_1 + 2P_2)$, plus the correction $\frac{3}{2}p$ due to jumping between ND$_2$ and ND$_3$ sites.

*The latter assumption is justified since the basis of the proposed mechanism is the experimental observation that deuterons of the ND$_2$ group relax via $P_1$ and $P_2$ much faster than the deuterons of the ND$_3$ group relax.*
APPENDIX C

Table XI and Fig. 34 summarize the recently available structural information\(^{(47)}\) on LiN\(_2\)D\(_5\)SO\(_4\). The N-D distances indicated in Table XI are not in good agreement with the N-H distances included in Table III. However, the general features of the structure are much the same.
### TABLE XI

**Bonded Distances**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
<th>Bond</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>S - O(1)</td>
<td>1.484</td>
<td>N(1)-D(1)</td>
<td>1.018</td>
</tr>
<tr>
<td>S - O(2)</td>
<td>1.487</td>
<td>N(1)-D(2)</td>
<td>1.030</td>
</tr>
<tr>
<td>S - O(3)</td>
<td>1.467</td>
<td>N(2)-D(3)</td>
<td>1.015</td>
</tr>
<tr>
<td>S - O(4)</td>
<td>1.476</td>
<td>N(2)-D(4)</td>
<td>1.022</td>
</tr>
<tr>
<td>N(1)-N(2)</td>
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<td>N(2)-D(5)</td>
<td>1.024</td>
</tr>
</tbody>
</table>

**Non-Bonded Distances**

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<th>Distance</th>
<th>Bond</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-O(1)'</td>
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<td>D(2)-N(1)'</td>
<td>2.042</td>
</tr>
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<td>Li-O(2)&quot;</td>
<td>1.993</td>
<td>D(3)-O(1)</td>
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<td>Li-O(3)</td>
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<td>D(4)-O(2)</td>
<td>1.932</td>
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<td>Li-O(4)</td>
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<td>D(5)-O(2)</td>
<td>2.064</td>
</tr>
</tbody>
</table>

' and " = related by symmetry operation
Fig. 34. Stereoscopic View of a Unit Cell of Li$_2$D$_2$SO$_4$. View Is Down c Axis with Positive a Axis to Right of Viewer. (After Ross and Hamilton(40))


41. F. Ross and W. Hamilton (private communication)
Hydrogen bonding in lithium hydrazinium sulfate