



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
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Abstract:

The nuclear magnetic resonance spectrum of deuterons in $\text{LiN}_2\text{D}_5\text{SO}_4$ has been studied in detail between 78 and 458°K. The spectrum at 78° is related to the deuterons of a static N_2D_5^{+} 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°K. Above 110°K the lines due to the deuterons of the ND_3 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 ND_2 group merge to a single pair between 0° and 50°C. These line mergers are related to the motion of the ND_3 and ND_2 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 ND_3 and ND_2 lines were measured over the temperature range from 155°K to 422°K. 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 ND_3 and ND_2 hindered rotations. In addition, evidence is found to indicate that jumping between ND_2 and ND_3 groups becomes important at temperatures above 75°C. None of the measurements discussed indicate that the crystal undergoes a ferroelectric transition below 200°C.

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ABSTRACT

The nuclear magnetic resonance spectrum of deuterons in $\text{LiN}_2\text{D}_5\text{SO}_4$ has been studied in detail between 78 and 458°K. The spectrum at 78° is related to the deuterons of a static N_2D_5^+ 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°K. Above 110°K the lines due to the deuterons of the ND_3 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 ND_2 group merge to a single pair between 0° and 50°C. These line mergers are related to the motion of the ND_3 and ND_2 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.

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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_2PO_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, $\sim 10^{-8}/\Omega$ 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, (10) and neutron diffraction studies (11) 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^7 nuclei in LiHzS have been carried out. (12,13) 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, $\text{LiN}_2\text{D}_5\text{SO}_4$, 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 determine 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 worthwhile. 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 ($\text{LiN}_2\text{H}_5\text{SO}_4$) has been studied by means of x-ray^(14,15,16) and neutron⁽¹¹⁾ diffraction. Table I compares the coordinates of the constituents of LiHzS found by these experiments.

LiHzS is orthorhombic of space group $\text{Pbn}2_1$,⁽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 $c=5.178 \text{ \AA}$. Brown⁽¹⁵⁾ has found for the cell dimensions $a=8.99$, $b=9.94$, and $c=5.18 \text{ \AA}$.*

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

| | | Brown ⁽¹⁵⁾ | Van den Hende & Boutin ⁽¹⁶⁾ | Padmanabhan & ⁽¹¹⁾ Balasubramanian | Standard ⁽¹¹⁾ Deviation |
|------|---|-----------------------|--|--|---------------------------------------|
| S | x | 0.1286 | 0.1290 | 0.126 | 0.001 |
| | y | 0.1579 | 0.1589 | 0.159 | 0.001 |
| | z | 0.250 | 0.250 | 0.250 | 0.002 |
| O(1) | x | 0.106 | 0.1068 | 0.106 | 0.002 |
| | y | 0.191 | 0.1870 | 0.193 | 0.001 |
| | z | 0.519 | 0.5434 | 0.533 | 0.002 |
| O(2) | x | 0.154 | 0.1511 | 0.153 | 0.002 |
| | y | 0.010 | 0.0132 | 0.012 | 0.001 |
| | z | 0.220 | 0.2296 | 0.229 | 0.001 |
| O(3) | x | 0.259 | 0.2558 | 0.259 | 0.001 |
| | y | 0.230 | 0.2335 | 0.230 | 0.001 |
| | z | 0.149 | 0.1626 | 0.151 | 0.002 |
| O(4) | x | 0.497 | 0.4904 | 0.498 | 0.001 |
| | y | 0.302 | 0.3048 | 0.304 | 0.001 |
| | z | 0.596 | 0.6016 | 0.600 | 0.002 |
| N(1) | x | 0.418 | 0.4193 | 0.414 | 0.001 |
| | y | 0.002 | 0.0285 | 0.024 | 0.001 |
| | z | 0.746 | 0.7405 | 0.743 | 0.002 |
| N(2) | x | 0.217 | 0.2137 | 0.213 | 0.001 |
| | y | 0.440 | 0.4460 | 0.440 | 0.001 |
| | z | 0.742 | 0.7346 | 0.739 | 0.002 |
| Li | x | 0.437 | 0.433 | 0.422 | 0.003 |
| | y | 0.332 | 0.339 | 0.336 | 0.003 |
| | z | 0.253 | 0.271 | 0.256 | 0.003 |
| H(1) | x | — | — | 0.381 | 0.004 |
| | y | — | — | 0.118 | 0.003 |
| | z | — | — | 0.796 | 0.003 |

TABLE I (continued)

| | | Brown(15) | Van den(16) Hende & Boutin | Padmanabhan &(11) Balasubramanian | Standard(11) Deviation |
|------|---|-----------|-------------------------------|--------------------------------------|---------------------------|
| H(2) | x | _____ | _____ | 0.467 | 0.004 |
| | y | _____ | _____ | 0.036 | 0.004 |
| | z | _____ | _____ | 0.571 | 0.004 |
| H(3) | x | _____ | _____ | 0.189 | 0.003 |
| | y | _____ | _____ | 0.345 | 0.003 |
| | z | _____ | _____ | 0.677 | 0.003 |
| H(4) | x | _____ | _____ | 0.247 | 0.005 |
| | y | _____ | _____ | 0.428 | 0.004 |
| | z | _____ | _____ | 0.924 | 0.004 |
| H(5) | x | _____ | _____ | 0.292 | 0.004 |
| | y | _____ | _____ | 0.469 | 0.002 |
| | z | _____ | _____ | 0.601 | 0.003 |

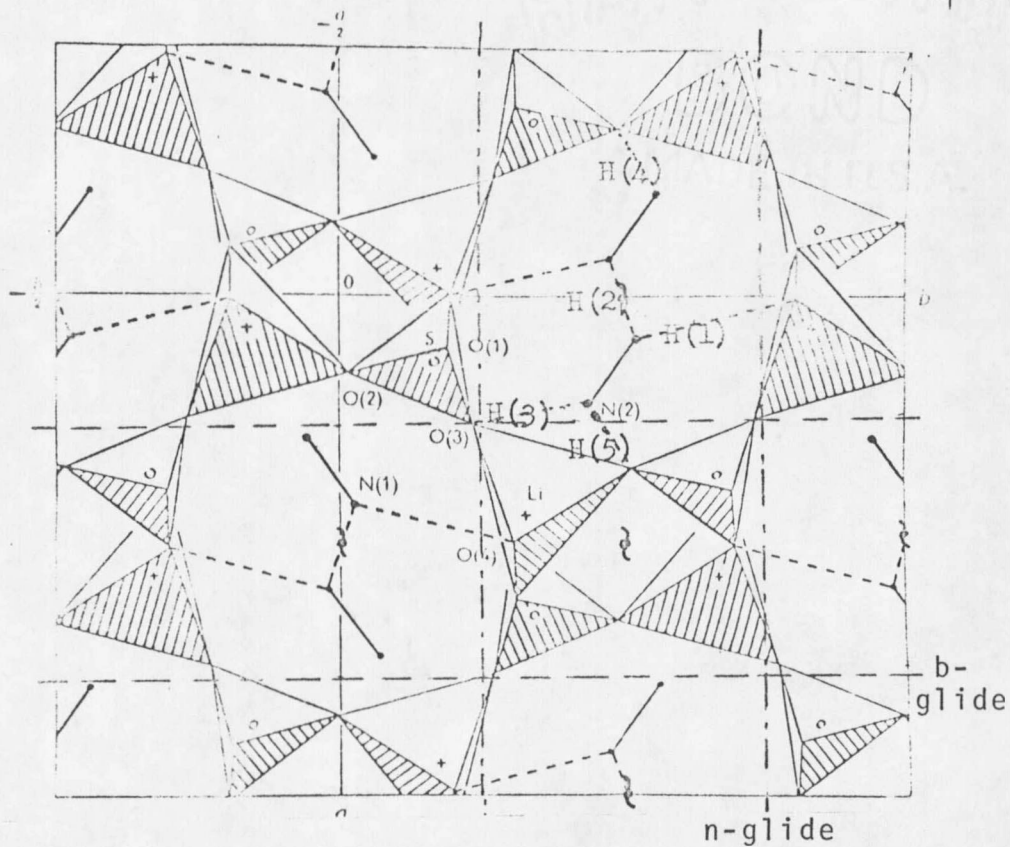


Fig. 1 A View of LiHzS Projected Down the c Axis.
(After Brown⁽¹⁵⁾)

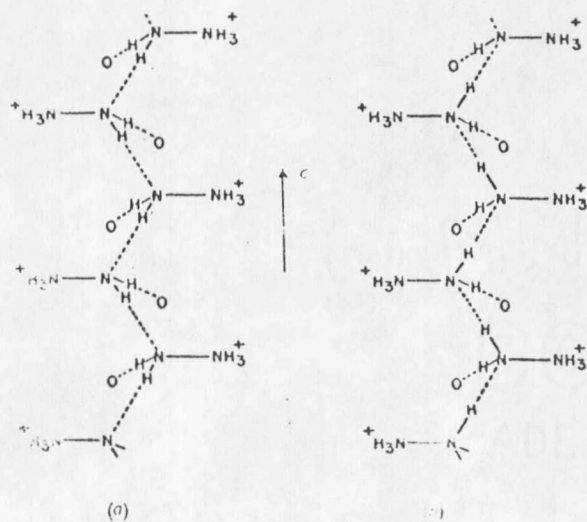


Fig. 2 Two Alternate Arrangements Possible for
 $\text{N-H}\dots\text{N-H}\dots$ Chain if the Hydrogen Bonds Are Ordered.
(After Brown⁽¹⁵⁾)

