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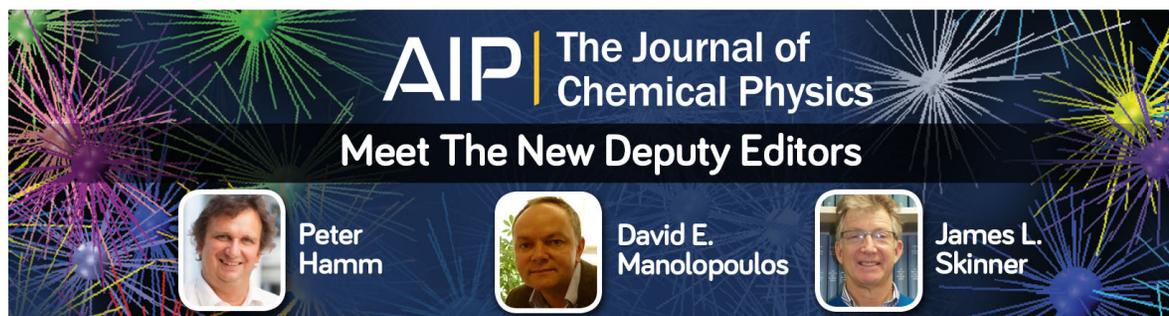
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## Deuteron NMR Study of Lithium Hydrazinium Sulfate\*

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The magnetic resonance spectrum of the deuterons in single crystals of  $\text{LiN}_2\text{D}_6\text{SO}_4$  has been studied between 78 and 458°K. The electric quadrupole coupling constants, the asymmetry parameters, and the orientations of the electric field gradient (efg) tensors relative to the crystal axes were obtained at 78°K, 193°K, 25°C, 65°C, and 95°C. The orientations of the efg tensors are considered in relation to nearby atomic sites. At 78°K the spectrum contains distinct lines due to the five deuterons of the  $\text{N}_2\text{D}_5^+$  ion. Between 110 and 150°K the lines due to the three deuterons of the  $\text{ND}_3$  group broaden and merge to a single pair which is still visible at 185°C. A small change with temperature in the coupling constant associated with this pair of lines is discussed. The lines due to the two deuterons of the  $\text{ND}_2$  group broaden and merge to a single pair between 0 and 50°C. These line mergers result from hindered rotation of the  $\text{ND}_2$  and  $\text{ND}_3$  groups. Estimates of the activation energies for these motions are made. These changes in the spectrum are related to the results of earlier NMR studies and to previous electrical conductivity and dielectric constant measurements.

## INTRODUCTION

A number of investigations on the structure and properties of  $\text{LiN}_2\text{H}_5\text{SO}_4$  (hereafter abbreviated as LiHzS) have been carried out since Pepinsky, Vedam, Okaya, and Hoshino<sup>1</sup> measured the ferroelectric properties in 1958. X-ray analyses were carried out by Brown<sup>2</sup> and by Van den Hende and Boutin,<sup>3</sup> and a neutron diffraction study of the structure was done by Padmanabhan and Balasubramanian<sup>4</sup> in 1966. Infrared and Raman studies of the crystal have been made by Warriar and Narayanan<sup>5</sup> and by Krishnan and Krishnan,<sup>6</sup> respectively. Electrical conductivities of both LiHzS<sup>7</sup> and the deuterated crystal LiDzS<sup>8</sup> have been measured.

The crystal contains four molecular units per unit cell, so there are four  $\text{N}_2\text{H}_5^+$  (hydrazinium) ions per cell. These are related by rotation and reflection symmetries.<sup>2</sup> The  $\text{NH}_2$  ends of these  $\text{N}_2\text{H}_5^+$  ions are linked by chains of  $\text{N-H}\cdots\text{N}$  bonds running along the  $c$  axis of the crystal which is the ferroelectric axis. Vanderkooy *et al.*<sup>7</sup> have shown the crystal to be a protonic conductor and these chains are probably related to the fact that the  $c$  axis conductivity observed in both the non-deuterated and deuterated crystals is much larger than the conductivity measured perpendicular to  $c$ . The other hydrogen of the  $\text{NH}_2$  end of the hydrazinium ion

and the three hydrogens of the  $\text{NH}_3$  end form  $\text{N-H}\cdots\text{O}$  bonds.

An NMR study was carried out by Cuthbert and Petch<sup>9</sup> over the temperature range  $-80^\circ\text{C}$  to above  $200^\circ\text{C}$ . They studied the linewidth of the proton signal and the quadrupolar splitting of the  $\text{Li}^{7}$  signal. The proton second moment shows a decrease above  $-183^\circ\text{C}$  which they attributed to hindered rotation of the  $\text{NH}_3$  groups. A further line narrowing between room temperature and  $200^\circ\text{C}$  was suggested to be due to rotation of  $\text{NH}_2$  groups and possible jumping of protons between  $\text{N}_2\text{H}_5^+$  ions or tumbling of these ions. Gradual changes in the quadrupole splitting spectrum of  $\text{Li}^{7}$  as the temperature was increased from  $-80$  to  $165^\circ\text{C}$  reflect a change in the framework of  $\text{LiO}_4$  and  $\text{SO}_4$  tetrahedra surrounding the  $\text{N}_2\text{H}_5$  chains in the crystal. Because of this, Cuthbert and Petch suggest that the crystal undergoes a phase change from a low- to high-temperature polymorph. Thermal expansion data of Devanarayanan and Easwaran<sup>10</sup> give added information on structure changes with temperature.

Pepinsky *et al.*<sup>1</sup> reported that a good hysteresis loop was observed between  $-15$  and  $80^\circ\text{C}$ , but they observed no dielectric peak between  $-196$  and  $140^\circ\text{C}$  and no specific-heat anomaly between  $-120$  and  $205^\circ\text{C}$ . We have found no dielectric peak up to  $205^\circ\text{C}$ .<sup>11</sup>

This study was undertaken in the hope that the motions and phase change suggested by Cuthbert and Petch might be clarified and thus that the ferroelectric property of the crystal might be better understood.

## EXPERIMENTAL

Well-developed single crystals of LiHzS are easily grown by controlled evaporation from water solution. The deuterated crystals were obtained by first growing single crystals of LiHzS by evaporation from a solution

<sup>9</sup> J. D. Cuthbert and H. E. Petch, *Can. J. Phys.* **41**, 1629 (1963).

<sup>10</sup> S. Devanarayanan and K. R. K. Easwaran, *Proc. Indian Acad. Sci.* **64A**, 173 (1966).

<sup>11</sup> F. L. Howell and V. H. Schmidt, *Bull. Am. Phys. Soc.* **13**, 876 (1968).

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<sup>1</sup> R. Pepinsky, K. Vedam, Y. Okaya, and S. Hoshino, *Phys. Rev.* **111**, 1467 (1958).

<sup>2</sup> I. D. Brown, *Acta Cryst.* **17**, 654 (1964).

<sup>3</sup> J. H. Van den Hende and H. Boutin, *Acta Cryst.* **17**, 660 (1964).

<sup>4</sup> V. M. Padmanabhan and R. Balasubramanian, *Acta Cryst.* **22**, 532 (1967).

<sup>5</sup> A. V. R. Warriar and P. S. Narayanan, *Proc. Indian Acad. Sci.* **64A**, 254 (1966).

<sup>6</sup> R. S. Krishnan and K. Krishnan, *Proc. Indian Acad. Sci.* **61A**, 122 (1965).

<sup>7</sup> J. Vanderkooy, J. D. Cuthbert, and H. E. Petch, *Can. J. Phys.* **42**, 1871 (1964).

<sup>8</sup> F. L. Howell, R. R. Knispel, and V. H. Schmidt, *Bull. Am. Phys. Soc.* **12**, 924 (1967).

TABLE I. Coupling constant  $eqQ/h$ , asymmetry parameter  $\eta$ , and the angle formed between the principal axis of the field gradient and the line between the nitrogen and proton involved in the bond. Also listed are the N-H...X bond angles and intrabond lengths calculated from the room temperature data of Padmanabhan and Balasubramanian (Ref. 4).

	Bond	$eqQ/h$ , kHz	$\eta$	$\phi_{zz}$ , N-H angle, deg.	N-H...X (H-bond) angle, deg.	H-bond dims. (Å)	
						N-H	H...X
$T=78^\circ\text{K}$	1	$208 \pm 1$	$0.16 \pm 0.07$	$9 \pm 1$	118.2	1.02	2.35
	2	$178 \pm 1$	$0.12 \pm 0.07$	$4 \pm 1$	156.4	1.02	2.09
	3	$166 \pm 1$	$0.05 \pm 0.07$	$10 \pm 1$	166.3	1.02	1.84
	4	$167 \pm 1$	$0.10 \pm 0.07$	$7 \pm 1$	146.1	1.01	2.00
	5	$162 \pm 1$	$0.05 \pm 0.07$	$1 \pm 1$	150.3	1.05	2.03
$T=193^\circ\text{K}$	1	$201 \pm 1$	$0.15 \pm 0.07$	$7 \pm 1$			
	2	$178 \pm 1$	$0.08 \pm 0.07$	$4 \pm 1$			

of  $\text{Li}_2\text{CO}_3$  and  $(\text{NH}_2)_2\text{H}_2\text{SO}_4$  in  $\text{H}_2\text{O}$ , then dissolving and recrystallizing twice, from 90.0%  $\text{D}_2\text{O}$  and from 99.8%  $\text{D}_2\text{O}$ . This final crystal growth from 99.8%  $\text{D}_2\text{O}$  was carried out in a desiccator to minimize water vapor exchange with the atmosphere. A Robinson circuit<sup>12</sup> and a transistorized spectrometer,<sup>13</sup> both operating at 14 MHz and employing frequency modulation at 1500 Hz, were used in conjunction with a phase sensitive detector and in some instances a signal averager to obtain the deuterium NMR spectra. Complete spectra for rotation about the three crystallographic axes were

measured at  $78^\circ\text{K}$ ,  $-80^\circ\text{C}$ , room temperature,  $65^\circ\text{C}$ , and  $95^\circ\text{C}$ . The temperature for the measurements near  $-80$ ,  $65$ , and  $95^\circ\text{C}$  was controlled to only  $\pm 5^\circ\text{C}$ . Since the quadrupolar splitting of the deuteron resonance lines is not sensitively dependent on the temperature at these temperatures this caused no significant increase in the experimental error. Measurements of the signal to noise ratio at particular orientations were made from room temperature to  $150^\circ\text{C}$ , with the temperature controlled to  $1^\circ\text{C}$ .

Alignment of a crystal axis to within  $0.5^\circ$  of the

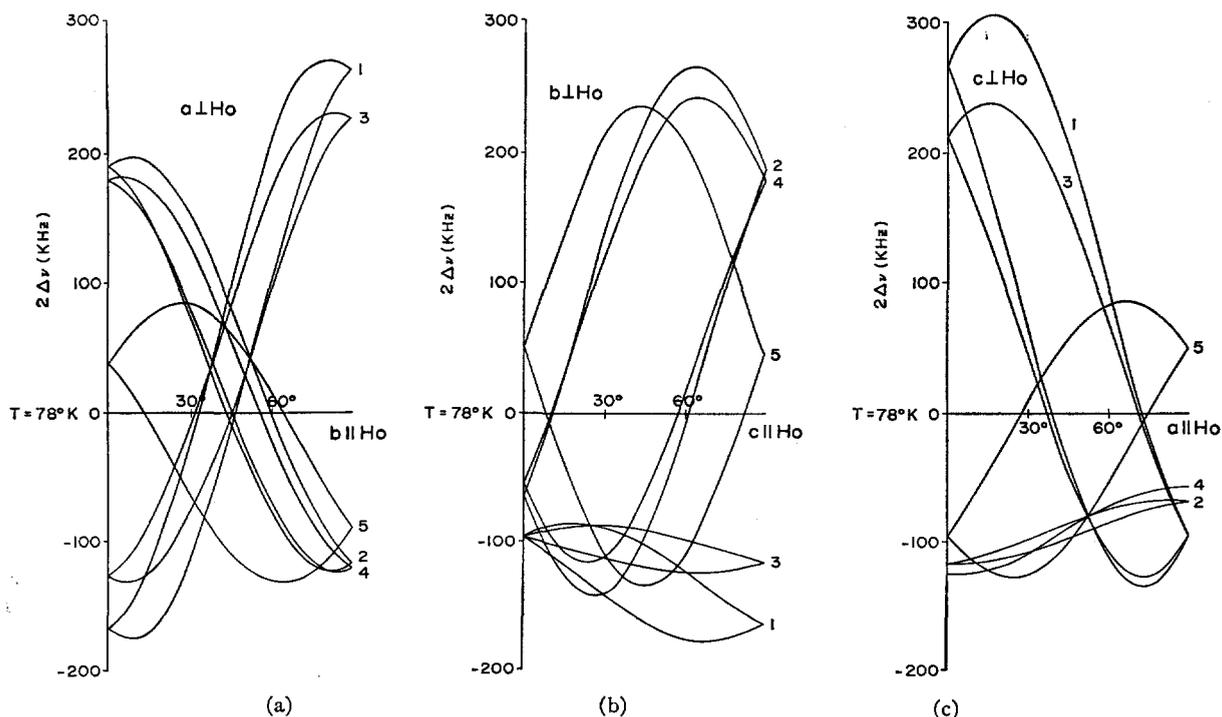


FIG. 1. Quadrupole splitting patterns for rotations about the three crystallographic axes at liquid-air temperature.

<sup>12</sup> F. N. H. Robinson, *J. Sci. Instr.* **36**, 481 (1959).

<sup>13</sup> F. J. Blankenburg, R. R. Knispel, and V. H. Schmidt, *Rev. Sci. Instr.* **37**, 1020 (1966).

TABLE II. Coupling constant  $eqQ/h$ , asymmetry parameter  $\eta$ , and the angles between the principal axes and the crystallographic axes for the efgs resulting from motional averaging over sites 1 and 2 and over sites 3-5. Calculated averages based on efgs measured at 78°K for individual sites are given for comparison.

	Temperature	$eqQ/h$ , kHz	$\eta$	$\theta_x$	$\theta_y$	$\theta_z$
Measured for average due to sites 3-5	-80°C	48.9±0.5	0.29±0.05	37.1±0.5	127.4±0.5	89.0±0.5
	25°C	48.6±0.5	0.22±0.05	38.0±0.5	127.5±0.5	89.9±0.5
	65°C	47.5±0.5	0.18±0.05	38.4±0.5	128.3±0.5	88.4±0.5
	95°C	46.3±0.5	0.16±0.05	39.1±0.5	129.0±0.5	87.6±0.5
Calculated average for sites 3, 4, and 5		51.0	0.46	36.9	126.7	88.5
Measured for average due to sites 1 and 2	95°C	91.0±3	0.90±0.15	64.0±2.0	52.0±2.0	131.0±2.0
Calculated average for sites 1 and 2		97.8	0.98	64.2	45.8	124.8

rotation axis was achieved by visually aligning the crystal faces, which are sharply defined. The simplification which occurs in the spectrum at orientations for which the magnetic field is parallel to a crystal axis provides a check on the initial alignment. The angle of rotation about a given axis was measured to 0.1° by means of a divided circle attached to the spectrometer.

For most of the rotations a spectrum was taken every 5°, and the data points were easily fit to sine curves by using an overlay. The data points scatter about the fitted curve by less than 1 kHz for regions of the rotation curves where no overlap of the spectral lines occurs. In all cases of significant overlap the corresponding data points were excluded. The 78°K rotation spectra were obtained at 2.5° intervals because at that temperature there are many lines and many points that must be excluded. The remaining points were fitted to the appropriate curves by a least-squares technique. The diagonal values of the field gradient tensors, coupling constants, asymmetry parameters, and the direction cosines of the principal axes relative to the crystal axes were obtained using the analysis of Volkoff, Petch, and Smellie.<sup>14</sup>

RESULTS

For arbitrary orientations of the crystal relative to the applied magnetic field  $H_0$  at 78°K, twenty pairs of deuteron lines are observed corresponding to the twenty deuterons per unit cell. These twenty deuterons are in four  $N_2D_6^+$  ions, which are related by the symmetries previously noted. These symmetries cause the spectrum for rotation about a crystal axis perpendicular to  $H_0$  to have only ten pairs of lines, and with  $H_0$  parallel to a crystal axis these merge to five pairs. Figure 1 shows the angular dependence of the splitting observed at 78°K for each of the five sites. The corresponding quadrupolar coupling constants, asymmetry parameters, and angles between each electric field gradient (efg) principal axis and the line joining that hydrogen to its nearest neighbor (a nitrogen in all cases) are given in Table I. These are given for all five nonequivalent sites at 78°K, with the sites numbered in accord with Padmanabhan and Balasubramanian.<sup>4</sup>

As the crystal is warmed above 100°K, the lines corresponding to sites 3-5 (the  $ND_3$  sites) broaden,

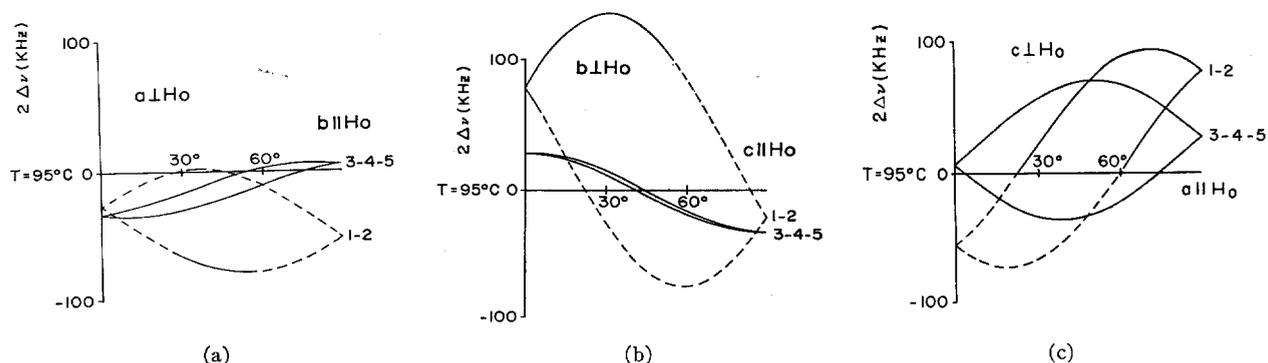


FIG. 2. Quadrupole splitting patterns of the two sets of averaged lines for rotations about the three crystallographic axes at 95°C. Dashed lines indicate regions in which the lines could not be observed.

<sup>14</sup> G. M. Volkoff, H. E. Petch, and D. W. L. Smellie, Can. J. Phys. 30, 270 (1952).

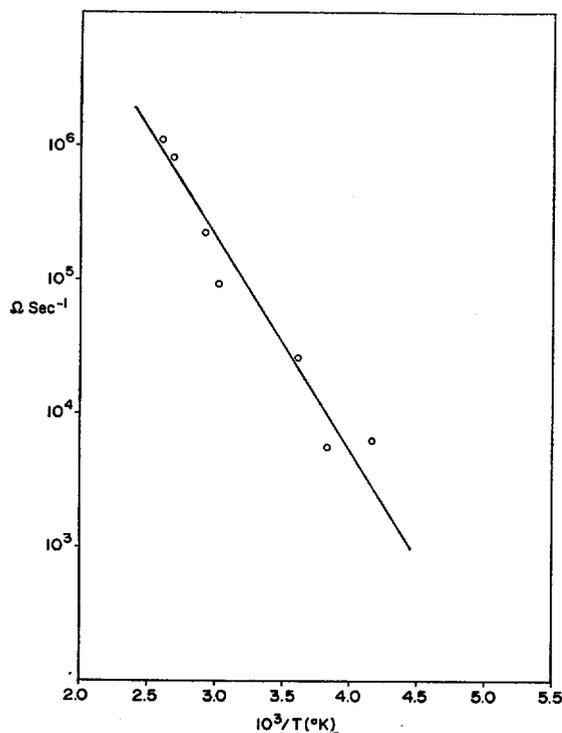


FIG. 3. Temperature dependence of the exchange probability  $\Omega$  for exchange between deuteron sites 1 and 2.

and disappear near 115°K. Above 140°K, a single pair of strong lines appears, corresponding to an average over sites 3–5. The spectrum due to this averaging changes very little with temperature and it is still evident at 185°C.

At approximately room temperature the lines due to sites 1 and 2 (the ND<sub>2</sub> sites) are broadened so that they are no longer visible. At 60°C, a new set of lines is observed in certain orientations, and these lines become stronger as the temperature is increased up to about 120°C. This set of lines is due to hindered rotation of the ND<sub>2</sub> groups. These lines appear only when the separation between lines over which the averaging takes place is less than about 65 kHz. The angular dependence of the splittings observed at 95°C is displayed in Fig. 2.

The measured coupling constants, asymmetry parameters, and angles of interest for these average efg's resulting from hindered rotations are given in Table II, together with corresponding calculated values obtained by forming two efg tensors having components which are the averages of the corresponding tensor components in the crystal system for the appropriate deuteron sites and then diagonalizing these tensors.

## DISCUSSION

We relate the deuteron efg results to the LiHzS structure, as the LiDzS structure has not been studied. The first principal axis, defined as the axis for the

largest efg tensor component, lies nearly along the N–H bond direction at each deuteron site. The largest angle formed between this axis and the corresponding N–H direction is 10° and occurs for bonds 1 and 3. The number 1 N–H···O bond has an H···O distance near the upper limit for a hydrogen bond,<sup>15</sup> and the bond is bent through a large angle.

The second principal axes, for the second-largest efg components, tend to lie perpendicular to the N<sub>1</sub>–N<sub>2</sub>–H planes. A similar result has been noted by Chiba<sup>16</sup> for O–H···O bonds. The angles between these second principal axes and the perpendiculars to these planes are 17°, 16°, 14°, 12°, and 5° for sites 1–5, respectively, with estimated error of ±3°. This large estimated error occurs because the efg tensors are nearly axially symmetric.

The angles given in Table II for the field gradients which result from motional averaging correspond to the hydrazinium ion containing the N<sub>1</sub> nitrogen for which the coordinates are given by Padmanabhan and Balasubramanian.<sup>4</sup> The values of  $eqQ/h$  for the averages over sites 3–5 show a small but consistent decrease of about 5% from –80 to +95°C. If all the contents of the unit cell were to expand at the same rate, the efg would vary as (lattice parameter)<sup>-3</sup>. Use of the average of the anisotropic thermal expansion coefficients over this temperature range as measured by Devanarayanan and Easwaran<sup>10</sup> yields an efg decrease of a little over 1% from –80 to +95°C. The remainder of the decrease has two possible origins, namely the increase with temperature in the amplitude of torsional oscillations of the ND<sub>3</sub> groups, and whatever structure change is responsible for the decrease in the difference between the quadrupolar splittings of the two <sup>7</sup>Li sites.<sup>9</sup> The direction of the first principal axis of this ND<sub>3</sub> average makes an angle of 3.6° at room temperature and 2.6° at 95°C with the N<sub>1</sub>–N<sub>2</sub> direction calculated from the neutron diffraction data which was obtained at room temperature.

The efg resulting from motional averaging over bonds 1 and 2 did not change measurably between 65° and 95°C and is given for 95°C only. Because of the limited angular range over which these lines could be observed, the estimated error is somewhat larger than for the D<sub>3</sub>–D<sub>4</sub>–D<sub>5</sub> average. The first principal axis of the D<sub>1</sub>–D<sub>2</sub> average efg lies within 2° of the plane defined by H<sub>1</sub>–N<sub>1</sub>–H<sub>2</sub> and within 4° of the line bisecting the H<sub>1</sub>–N<sub>1</sub>–H<sub>2</sub> angle.

Values found for  $eqQ/h$  range 162–208 kHz for N–H···X distances of 2.84–3.06 Å. For O–D···O bonds with coupling constants in this range the corresponding O···O distances are about 2.6–2.8 Å. Blinc and Hadzi<sup>17</sup> have plotted coupling constants against

<sup>15</sup> G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (W. H. Freeman and Co., San Francisco, Calif., 1960), pp. 285–293.

<sup>16</sup> T. Chiba, *J. Chem. Phys.* **41**, 1352 (1964).

<sup>17</sup> R. Blinc and D. Hadzi, *Nature* **212**, 1307 (1966).

the squares of the corresponding O-H stretching frequencies. An approximately linear relation is evident, and we find that the coupling constants for LiDzS as functions of the N-H stretching frequencies determined from the Raman spectra results of Krishnan and Krishnan<sup>6</sup> lie along this line.

We have used a method described by Abragam<sup>18</sup> and Chiba<sup>19</sup> to estimate the rates of hindered rotation for the ND<sub>2</sub> group from measurements of the signal-to-noise ratio ( $S/N$ ) as a function of temperature. The linewidth  $W$  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  $T$ . (Thermal noise in the sample coil does not contribute significantly to  $N$  in these measurements.) The proportionality constant  $C$  was obtained at a low temperature for which the lines were unbroadened by the motion of interest. The linewidth used to find  $C$  was measured by multiplying the frequency corresponding to the distance between the points of zero slope on the recorded derivative curve by the factor appropriate for a Lorentzian line shape. The unbroadened line is assigned a linewidth  $\Delta$ , the line separation is  $2\delta$ , and the exchange probability is  $\Omega$ . Making the approximations that  $\Omega$  is much less than  $2\delta$  below the temperature region of extreme broadening, and much larger than  $2\delta$  above the region, gives the following equations for the absorption  $I(\omega)$ :

$$I(\omega) = (\Omega + \Delta) / [(\omega \mp \delta)^2 + (\Omega + \Delta)^2], \quad \text{low temperature;}$$

$$I(\omega) = \frac{2[(\delta^2/2\Omega) + \Delta]}{\omega^2 + [(\delta^2/2\Omega) + \Delta]^2}, \quad \text{high temperature;}$$

with the corresponding linewidths

$$W_{LT} = \Omega + \Delta, \quad \text{low temperature;}$$

$$W_{HT} = (\delta^2/2\Omega) + \Delta, \quad \text{high temperature.}$$

From the linewidths  $\Omega$  is calculated and appears in Fig. 3. If  $\Omega = \Omega_0 \exp(-E_0/kT)$ , the slope of Fig. 3 gives a value of 0.31 eV for the activation energy of the motion. Within experimental error this activation energy is the same as that found<sup>11</sup> from dielectric constant measurements on LiDzS from 5 to 10<sup>6</sup> Hz and from 30 to 160°C, after subtracting the dielectric constant contribution having activation energy 0.75 eV.

<sup>18</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), pp. 447-451.

<sup>19</sup> T. Chiba, *J. Chem. Phys.* **39**, 947 (1963).

Thus it appears likely that the ND<sub>2</sub> hindered rotation is related to the low activation energy contribution to the dielectric constant. The 0.75-eV contribution may be related to the dc conductivity mechanism for which we found an activation energy of 0.65 eV in LiDzS,<sup>8</sup> as compared with the value 0.85 eV found for LiHzS.<sup>7</sup>

Hindered rotation of the ND<sub>3</sub> group becomes important at a much lower temperature. Preliminary deuteron spin-lattice relaxation time measurements<sup>20</sup> give an activation energy in the neighborhood of 0.20 eV. This is quite close to the value of 4.2 kcal/mole (0.18 eV) found for NH<sub>3</sub> hindered rotation in LiHzS by MacClement, Pintar, and Petch.<sup>21</sup>

## CONCLUSION

The deuteron spectra at low temperature yield efg tensors which are in good agreement with what one would expect on the basis of the proton locations found by neutron diffraction. We have shown that hindered rotations of the ND<sub>3</sub> and ND<sub>2</sub> groups occur, as was indicated by the previous proton NMR studies, and have found approximate activation energies for these motions. The presence of the ND<sub>3</sub> merged lines at 185°C implies that the conductivity is due primarily to the ND<sub>2</sub> deuterons, that the second-order phase transition which is completed at 164°C has little effect on the ND<sub>3</sub> groups, and that if the hydrazinium ion tumbles, as has been previously speculated, this motion is not rapid at 185°C.

The neutron diffraction study indicates that the protons in the N-H...N bonds are ordered in the upper or + $c$  ends of the bonds. The deuteron NMR spectra show no extra lines which could arise if some deuterons were in the lower ends of these bonds due to disorder or ferroelectric domain effects. The structure is such that one cannot reasonably expect it to reverse along the ferroelectric ( $c$ ) axis upon domain reversal. We are initiating NMR measurements on crystals subjected to large electric fields at low temperatures to try to determine what structural changes accompany domain reversal.

## ACKNOWLEDGMENT

The authors wish to thank Mr. Roy Knispel for his assistance with the data analysis.

<sup>20</sup> R. S. Parker (private communication).

<sup>21</sup> W. D. MacClement, M. Pintar, and H. E. Petch, *Can. J. Phys.* **45**, 3257 (1967).