

# Nuclear Quadrupole Resonance of Li in Ferroelectric Compounds

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Measurements have been made of the temperature dependence of the nuclear quadrupole coupling constant,  $eQq/h$ , of Li in a number of ferroelectric compounds. The compounds discussed are  $\text{LiNH}_4\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ ,  $\text{LiTiC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ ,  $\text{LiTaO}_3$ ,  $\text{LiNbO}_3$ , and  $\text{LiN}_2\text{H}_5\text{SO}_4$ . Powdered samples were used in all cases except the first where single crystals were also measured and favorably compared with the powder results.

## INTRODUCTION

THE nuclear quadrupole coupling constant  $eQq/h$  has been measured in a number of solids.<sup>1</sup> The field gradient  $q$ , which is the second derivative of the electrostatic potential along a principal axis  $\partial^2 V/\partial z^2$ , can give information about the electronic environment of the nucleus studied. If the temperature dependence of  $eQq/h$  is studied, then changes in  $q$  can be observed. For Li in ionic solids  $eQq/h$  is usually small ( $\approx 100$  kc/sec). This is so because the nuclear quadrupole moment  $Q$  of  $\text{Li}^7$  is relatively small.<sup>2</sup> In addition, the enhancement factor<sup>3</sup> that plays an important role in determining  $q$  is less than 1,<sup>4</sup> rather than being  $\gg 1$  as it is for ions that have  $p$  and  $d$  electrons.<sup>3,5</sup>

Since  $eQq/h$  is small, it can be obtained by performing a nuclear magnetic resonance (NMR) experiment on the  $\text{Li}^7$  nuclei and observing the satellite lines. If the experiment is done in a single crystal, the five unknowns can be found,<sup>1</sup> namely:  $eQq/h$ , the asymmetry parameter,  $\eta$ ,<sup>6</sup> and the angles that describe the orientation of the field gradient tensor with respect to the crystal axes. However, the experiment can be done on a powder in which case only  $eQq/h$  and  $\eta$  can be found. Even then the data do not allow one to get values as accurately as can be obtained from single crystals. For some compounds the powder method is the only way to find  $eQq/h$ , since single crystals are difficult to obtain.

Pound first observed the pattern that occurs for Li NMR spectra with a small quadrupole splitting.<sup>7</sup> Hon and Bray<sup>8</sup> have obtained  $eQq/h$  and  $\eta$  values for

Li in a number of compounds. Silver and Bray have studied  $\text{B}^{11}$   $eQq/h$  by the powder method and have applied it to study glasses<sup>9</sup> and  $\text{B}_4\text{C}$ .<sup>10</sup> Other compounds have been studied by this method<sup>11</sup> including measurements of  $eQq/h$  of Be in the metal.<sup>12</sup> Recently, the similarity between the quadrupole Hamiltonian and certain types of electron spin Hamiltonians has been exploited to extend the powder work to electron spin resonance.<sup>13</sup>

The compounds that are studied here are ferroelectric; thus, it is of interest to try to relate the changes in the ferroelectric properties to  $eQq/h$ . These changes are perhaps more interesting than accurate values of  $eQq/h$  since the theory of  $Q$  and  $q$  is not nearly as sophisticated as the experiment.

Thus, the objects of this work are as follows: (1) To better understand the powder pattern with respect to the single-crystal results (complete single-crystal results in one case have been measured and compared to the powder results); (2) to obtain  $eQq/h$  and  $\eta$  for  $\text{Li}^7$  in a number of ferroelectrics that contain Li; (3) to compare the values obtained with structural data when it exists; (4) to study the temperature dependence of  $eQq/h$  so that changes that can possibly be related to the onset of ferroelectricity or the change in spontaneous polarization, can be understood.

## THEORY

The theoretical shape function for a NMR line in powders to which one adds a nuclear quadrupole coupling to first order was worked out by Feld and Lamb<sup>14</sup> and applied by Pound.<sup>7</sup> Their shape function applies when the nucleus sees axial symmetry ( $\eta=0$ ). The shape function that arises when  $\eta \neq 0$ , but the nuclear quadrupole coupling is still considered as a first-order perturbation on the NMR levels, was worked out by

<sup>1</sup> For general references to the field of nuclear quadrupole resonance see: M. H. Cohen and F. Reif, *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 5; and T. P. Das and E. L. Hahn, *ibid.*, Suppl. 1.

<sup>2</sup> For a list of values of nuclear quadrupole moments and references to the original work see: C. H. Townes, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958). See also G. Burns, *Phys. Rev.* **115**, 357 (1959); S. L. Kahalas and R. K. Nesbet, *ibid.* Letters **6**, 549 (1961).

<sup>3</sup> H. M. Foley, R. M. Sternheimer, and D. Tycko, *Phys. Rev.* **93**, 734 (1954); R. M. Sternheimer and H. M. Foley, *ibid.* **102**, 731 (1956); R. M. Sternheimer, *ibid.* **84**, 244 (1951).

<sup>4</sup> T. P. Das and R. Bersohn, *Phys. Rev.* **102**, 733 (1956).

<sup>5</sup> A short but probably adequate review of  $\gamma_\infty$  results can be found: G. Burns and E. G. Wikner, *Phys. Rev.* **121**, 155 (1961).

<sup>6</sup> The asymmetry parameter  $\eta$  is defined as  $(q_{xx} - q_{yy})/q_{zz}$ . Thus,  $\eta=0$  for axial symmetry.

<sup>7</sup> R. V. Pound, *Phys. Rev.* **79**, 685 (1950).

<sup>8</sup> J. F. Hon and P. J. Bray, *Phys. Rev.* **110**, 624 (1958).

<sup>9</sup> A. H. Silver and P. J. Bray, *J. Chem. Phys.* **29**, 984 (1958).

<sup>10</sup> A. H. Silver and P. J. Bray, *J. Chem. Phys.* **31**, 247 (1959).

<sup>11</sup> A. H. Silver and P. J. Bray, *J. Chem. Phys.* **32**, 288 (1960); A. H. Silver, *ibid.* 959 (1960); M. E. Milberg, R. K. Belitz, and A. H. Silver, *Phys. and Chem of Glasses* **1**, 155 (1960); P. J. Bray, J. O. Edwards, J. G. O'Keefe, V. F. Ross, and I. Talsuzaki, *J. Chem. Phys.* **35**, 435 (1961); J. F. Hon, *Phys. Rev.* **124**, 1368 (1961).

<sup>12</sup> W. D. Knight, *Phys. Rev.* **92**, 539 (1954).

<sup>13</sup> G. Burns, *J. Appl. Phys.* **32**, 2048 (1961).

<sup>14</sup> B. T. Feld and W. E. Lamb, *Phys. Rev.* **67**, 15 (1945).

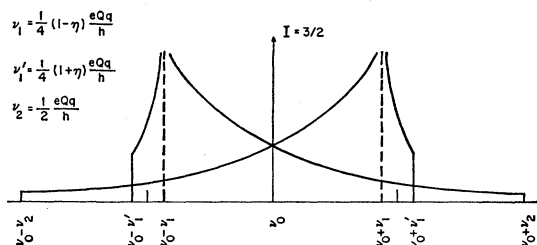


FIG. 1. The NMR line shape (references 14, 15) for first-order nuclear quadrupole splitting for a nonzero asymmetry parameter  $\eta$ . The nuclear spin  $I = 3/2$ .

Bloembergen and Rowland<sup>15</sup> and applied by Cohen and Reif.<sup>1</sup> The result is pictured in Fig. 1. There is a large peak in the absorption curve at  $\nu_0 \pm \nu_1$  and two small discontinuities at  $\nu_0 \pm \nu_2$  and at  $\nu_0 \pm \nu_1'$ . The very large  $\pm 1/2 \leftrightarrow \mp 1/2$  line at  $\nu_0$ , which is undisplaced to first order in  $eQq/h$ , is indicated by a vertical arrow. As  $\eta$  approaches zero the lines at  $\nu_0 \pm \nu_1$  and  $\nu_0 \pm \nu_1'$  come together and are separated from  $\nu_0$  by  $\frac{1}{4}eQq/h$ . The lines at  $\nu_0 \pm \nu_2$  are separated from  $\nu_0$  by  $\frac{1}{2}eQq/h$ .

In practice six satellites are not observed. Rather one distinct pair is seen corresponding to an average of  $\nu_0 \pm \nu_1$  and  $\nu_0 \pm \nu_1'$  (except in one case reported here where the lines at  $\nu_0 \pm \nu_2$  were observed) or a pair with some structure is seen.<sup>8</sup> It becomes a slight art to recognize a  $\eta = 0$  pattern from a  $\eta \neq 0$ . Clearly for small  $\eta$  this cannot be done. However, when the nucleus lies on a site of axial symmetry,  $\eta = 0$ . Thus, if the structure has been done one can tell if  $\eta = 0$  is expected. In practice, the spectrum for very small  $\eta$  ( $\eta \lesssim 0.1$ ) should be difficult to distinguish from  $\eta = 0$ . For very large  $\eta$  ( $\eta \gtrsim 0.6$ ), the line at  $\nu_0 \pm \nu_1$  will probably be lost in the very large line at  $\nu_0$ . If a satellite is then observed, it will be the sum of the lines at  $\nu_0 \pm \nu_1$  and  $\nu_0 \pm \nu_2$  and will be very small compared to the main line. Single-crystal measurements<sup>16</sup> of Li in  $\text{LiAl}(\text{SiO}_3)_2$  indicated  $\eta = 0.79$  and Hon and Bray<sup>8</sup> have observed the very small broad satellite that is then expected in this case. In the intermediate range of  $\eta$  the satellites again are large but not as distinct as in the  $\eta$  small case.

### EXPERIMENTAL

The measurements were made at 17 Mc/sec using a Pound-Knight-Watkins spectrometer<sup>17</sup> capable of operating at very low rf levels,<sup>18</sup> and a 12-in. Varian magnetic. The experimentally determined results are the derivatives of the absorption curves. In all cases, except one, no effects were seen due to  $T_1$  becoming excessively long. In the case of  $\text{LiN}_2\text{H}_5\text{SO}_4$ , the Li

resonance disappeared at  $-196^\circ\text{C}$ . However, irradiating with x rays at room temperature apparently shortened  $T_1$  enough so the resonance could be observed at  $-196^\circ\text{C}$  and no change in the room temperature results could be detected.

### RESULTS

One important consideration is line broadening and its effect on the powder pattern. It is not obvious if  $\nu_0 \pm \nu_1$  corresponds to a maximum or a zero in the experimentally measured derivative curve when magnetic dipole-dipole and other broadening effects are added to the theoretical pattern in Fig. 1. To answer this question, complete single-crystal data were taken on  $\text{Li}^{7}$  in  $\text{LiNH}_4(\text{tartrate}) \cdot \text{H}_2\text{O}$  and compared to the powder pattern. This will be described in detail in one of the following sections. In this case it is found that  $\eta = 0$ . Comparison with the powder shows that neither the peak nor the zero in the derivative curve corresponds to  $\nu_0 \pm \nu_1$ . Rather  $\frac{1}{4}(eQq/h)$  lies somewhere between the peak and the zero about 6 kc/sec closer to  $\nu_0$  than the peak in the derivative curve. Thus, values of  $\frac{1}{4}eQq/h$  were obtained from the data for the measurements reported here by subtracting 6 kc/sec from the separation of  $\nu_0$  to the peak in the experimental derivative curve.

To further check the correspondence of  $\nu_0 \pm \nu_1$  to the observed powder pattern, the Al resonance in  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  was observed at  $-196^\circ\text{C}$  and compared to the value measured in single crystals.<sup>19</sup> The conclusions are similar to those stated above.

### $\text{LiNH}_4\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ (LAT)

LAT is ferroelectric below  $-167^\circ\text{C}$ .<sup>20</sup> Some preliminary x-ray work on its room temperature structure has been done.<sup>21</sup> It is orthorhombic; space group  $P2_12_12_1$ ; cell content 4 formula units.

Nuclear quadrupole resonance (NQR) single-crystal data were obtained for rotations about the  $a$ ,  $b$ , and  $c$  crystallographic axes at several temperatures. The data was analyzed in the usual manner of Volhff *et al.*<sup>22</sup> The results are  $eQq/h = 93$  kc/sec and  $\eta = 0$ . One of the principal axes of the field gradient tensor is parallel to the  $b$  axis. The axis with the largest value of the field gradient is in the  $ac$  plane  $\pm 20$  deg with respect to the  $c$  axis. These values are independent of temperature between  $-196^\circ\text{C}$  and room temperature. The powder pattern was also measured and can be seen in Fig. 2. It is a typical  $\eta = 0$  pattern (or  $\eta \lesssim 0.1$ ). Since  $eQq/h$  is known from the single-crystal work, the rela-

<sup>15</sup> N. Bloembergen and T. J. Rowland, *Acta Met.* **1**, 731 (1953); T. J. Rowland, *ibid.* **3**, 74 (1955).

<sup>16</sup> G. M. Volkoff, H. E. Petch, and D. W. L. Smellie, *Can. J. Phys.* **30**, 270 (1952).

<sup>17</sup> R. V. Pound and W. D. Knight, *Rev. Sci. Instr.* **21**, 219 (1950); and R. V. Pound, *Progress in Nuclear Physics* (Butterworths-Springer, London, 1952), Vol. 2, p. 21.

<sup>18</sup> Capacitive rather than resistive feedback in the oscillator circuit seems to facilitate very low level operation.

<sup>19</sup> G. Burns, *J. Chem. Phys.* **32**, 1585 (1960).

<sup>20</sup> B. T. Matthias and J. K. Hulm, *Phys. Rev.* **82**, 108 (1951).

<sup>21</sup> R. C. Vernon and R. Pepinsky, final report, Contract DA-36-039-SC-21, Signal Corps Engineering Laboratories, 1953 (unpublished).

<sup>22</sup> See reference 16. Also G. M. Volkoff, *Can. J. Phys.* **31**, 820 (1953).

tion between  $\nu_0 \pm \nu_1$  and the powder pattern can easily be obtained as already discussed.

The lack of any change of  $eQq/h$  or  $\eta$  in going through the ferroelectric Curie point is at first sight surprising. In Rochelle salt ( $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ), which is not isomorphous with LAT but has a similar structure,<sup>23</sup> the structure work by Pepinsky and his co-workers,<sup>23</sup> indicates that the ferroelectric phenomenon is associated with the rotation of an O-H group and a slight shift of charge in the  $\text{C}_4\text{H}_4\text{O}_6$  ion. If such subtle effects also cause ferroelectricity in LAT, it is easily conceivable that the effect on  $q$  of Li would be small. The results will be more meaningful when the position of Li in the unit cell can be found and structural data are more complete.

### $\text{LiTiC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ (LTT)

LTT is isomorphous with LAT in its high temperature form<sup>24</sup> and becomes ferroelectric<sup>20</sup> at 10°K. However, the ferroelectric axis in LTT is the  $a$  axis while in LAT it is the  $b$  axis. The powder pattern of the Li NMR was measured between  $-196^\circ\text{C}$  and room temperature. It was the same as the LAT pattern within experimental error. Thus, the Li positions in the two compounds are undoubtedly the same. This is a further indication of the isomorphism of the two compounds in the high temperature phase which can not be found easily from the x-ray data since Li scatters x rays very weakly; i.e., the position of Li in LAT has not been determined.

### $\text{LiTaO}_3$

$\text{LiTaO}_3$  is a peculiar ferroelectric. Its spontaneous polarization ( $P_s$ ) increases with increasing temperature rather than decreases.<sup>25</sup> In fact,  $P_s$  is reported to be  $\approx 2 \mu\text{C cm}^{-2}$  at room temperature but begins to rise rapidly at  $\approx +225^\circ\text{C}$ .<sup>25</sup> At  $+440^\circ\text{C}$ ,  $P_s \approx 23 \mu\text{C cm}^{-2}$ . Rather than this decrease in  $P_s$  with decreasing temperature this behavior has sometimes been viewed as an increase in coercive field with decreasing temperature.<sup>26</sup> The powder pattern was observed between  $-196$  and  $+325^\circ\text{C}$ . This pattern (see Fig. 2) is a typical  $\eta=0$  pattern which is to be expected from the structure.

The signal-to-noise ratio of the Li resonance was very large and at  $-196^\circ\text{C}$  the lines due to  $\nu_0 \pm \nu_2$  were seen. In Fig. 2 the right-hand pattern plainly shows the resonance due to the  $\nu_0 \pm \nu_1$  and  $\nu_0 \pm \nu_2$  satellites. The

<sup>23</sup> C. A. Beevers and W. Hughes, Proc. Roy. Soc. (London) **A177**, 251 (1941); B. C. Frazer, M. McKeown, and R. Pepinsky, Phys. Rev. **94**, 1435 (1954); and R. Pepinsky (private communication).

<sup>24</sup> G. Shirane, F. Jona, and R. Pepinsky, Proc. Inst. Radio Engrs. **43**, 1738 (1955).

<sup>25</sup> B. T. Matthias and J. P. Remerka, Phys. Rev. **76**, 1886 (1949).

<sup>26</sup> H. D. Megaw, *Ferroelectricity in Crystals* (Methuen and Company, Ltd., London, 1957).

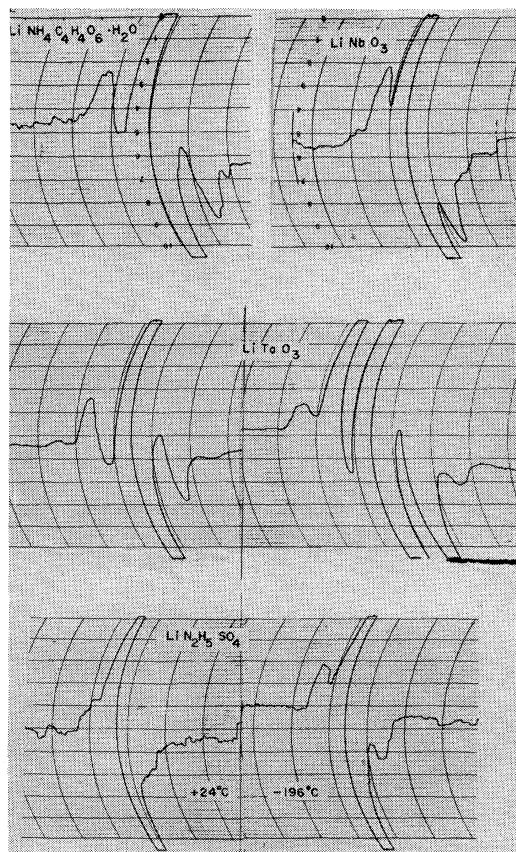


FIG. 2. Derivatives of the Li NMR absorption curves for the various compounds discussed in the text.

splittings between the satellites agree with the theory as summarized in Fig. 1.

Between  $-196$  and  $+235^\circ\text{C}$ ,  $eQq/h = 81 \text{ kc/sec}$ . At  $+325^\circ\text{C}$ , it increased to  $94 \text{ kc/sec}$ . Thus,  $eQq/h$  becomes larger in the same region where  $P_s$  increases. However, for such large increases in  $P_s$ , one would expect much larger increases in  $eQq/h$ . For example, in the tetragonal phase of  $\text{KNbO}_3$ , Hewitt<sup>27</sup> has shown that  $q$  of Nb  $\propto P^2$  for an ionic model. While the resonance measurements indicate that  $P_s$  may well increase with increasing temperature, they are not really consistent with such large changes in  $P_s$  as have been reported.

### $\text{LiNbO}_3$

This compound is ferroelectric<sup>25</sup> and isomorphous with  $\text{LiTaO}_3$ . Again  $P_s$  is reported to increase with increasing temperature but the sharp rise sets in at higher temperatures than  $200^\circ\text{C}$ .<sup>25</sup> The NQR measurements were made between  $-196$  and  $+150^\circ\text{C}$ . For some reason the signal-to-noise ratio was smaller in this compound than in the Ta compound. Again the sharp satellite indicates  $\eta=0$ , which is expected from the structure. A value of  $eQq/h = 46 \text{ kc/sec}$  independent of

<sup>27</sup> R. R. Hewitt, Phys. Rev. **121**, 45 (1961).

temperature is obtained. A partially complete room temperature structure has been worked out for  $\text{LiNbO}_3$ .<sup>28</sup> One of the unknowns is the sign of the parameter describing the Nb position with respect to the Li parameter. A calculation of the field gradient  $q$  at the Li site was made using the usual ionic crystal assumption:

$$q = (1 - \gamma_\infty) \sum_i [(3 \cos^2 \theta - 1)/r_i^3] e_i. \quad (1)$$

This has been successful in explaining the temperature dependence of  $eQq/h$  of Nb in  $\text{KNbO}_3$ .<sup>27</sup> In Eq. (1),  $\gamma_\infty$  is the shielding factor<sup>3</sup> for Li and the sum over all the  $i$  ions in the lattice with charge  $e_i$ . The lattice sum was performed on an IBM 704, using a program developed by Bersohn.<sup>29</sup> The results are in Table I. As can be seen, the quadrupole resonance results are much more consistent with the x-ray determination that results in the larger Nb-Li distance.

### $\eta \neq 0$ Compounds

In the powders studied so far it was known that  $\eta = 0$  from either the structure or single-crystal work. Also the powder patterns showed sharp large satellites indicating  $\eta \approx 0$ . In  $\text{LiTaO}_3$  the measurement of the lines at  $\nu_0 \pm \nu_2$  is a stringent further check on the data.

There are two Li containing ferroelectrics,  $\text{LiH}_3(\text{SeO}_3)_2$  and  $\text{LiN}_2\text{H}_5\text{SO}_4$ , for which the powder pattern indicates  $\eta \neq 0$ . Thus, the powder results will not be accurate; still changes in the pattern can easily be seen.

However, Anderson<sup>30</sup> has done careful single-crystal work on  $\text{LiH}_3(\text{SeO}_3)_2$ . His accurate measurements enable changes to be observed in  $eQq/h$  that are too small to be seen in powders. Thus, there is no need to discuss the powder results.<sup>31</sup>

$\text{LiN}_2\text{H}_5\text{SO}_4$  has been measured. The spontaneous polarization of this ferroelectric compound<sup>32</sup> is observed to increase from  $0.05 \mu\text{C cm}^{-2}$  at  $-10^\circ\text{C}$  to  $0.75 \mu\text{C cm}^{-2}$  at  $+70^\circ\text{C}$ .<sup>32</sup> However, no dielectric or thermal anomalies are observed. The resulting powder patterns

TABLE I. The results for the calculation of the lattice sum of Eq. (1) for Li in  $\text{LiNbO}_3$ . The contribution to the sum is listed for each of the ions in the lattice. For Nb,  $u = \pm 0.02$  was used since it is not known which should apply. See reference 28 for the values of the atomic parameters. To obtain  $q$  in the usual units ( $\text{esu/cm}^3$ ) one must multiply the total lattice sum by  $4.8029 \times 10^{-10}$  esu and  $(1 - \gamma_\infty)$ ,<sup>4</sup> and divide it by the cube of the unit cell dimensions ( $a = 5.492 \text{ \AA}$ ). To calculate  $eQq/h$ ,  $Q = 0.016 \times 10^{-24} \text{ cm}^2$  was used.<sup>2</sup>

Ion	Position	Results for lattice sum	
$\text{O}^{2-}$	$\pm(x, \frac{1}{2}-x, \frac{1}{4})$ , $x=0.628$	(+11.8092)	
$\text{Li}^{+1}$	$(u, u, u)$ ; $(\frac{1}{2}+u, \frac{1}{2}+u, \frac{1}{2}+u)$ , $u=0.18$	(+0.7142)	
$\text{Nb}^{+5}$	$(u, u, u)$ ; $(\frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}-u)$ , $ u =0.02$	(+2.0883)	( $u = -0.02$ )
		(+74.8967)	( $u = +0.02$ )
	$eQq/h = -36 \text{ kc/sec}$	( $u = -0.02$ )	
	$= -222 \text{ kc/sec}$	( $u = +0.02$ )	

at two temperatures are shown in Fig. 2. At  $-196^\circ\text{C}$  the pattern again looks as though  $\eta$  is small. The result was  $eQq/h \approx 54 \text{ kc/sec}$  and  $\eta$  small ( $\approx 0.1$ ). Possibly, between  $-196$  and  $-50^\circ\text{C}$ ,  $eQq/h$  increased slightly (the dip between the satellite and the main line got a bit smaller). Between  $-50$  and  $+123^\circ\text{C}$  the pattern developed into the one pictured in the figure for  $+23^\circ\text{C}$ . Thus,  $\nu_0 \pm \nu_1$  moved in and  $\nu_0 \pm \nu_1'$  moved out slightly. Thus,  $\eta$  increased to  $\approx 0.4$  and  $eQq/h$  decreased. This appeared to go on continuously and no sharp changes were seen.

When the sample was cooled from  $-119$  to  $-196^\circ\text{C}$  the Li resonance disappeared but reappeared when the sample was warmed to  $-119^\circ\text{C}$  again. Putting the sample in an x-ray beam for three days and then quickly cooling it to  $-196^\circ\text{C}$  made the resonance observable. It is known that this treatment produces many paramagnetic centers.<sup>33</sup> Thus,  $T_1$  was shortened and the resonance was observable. The proton NMR was observed to broaden between  $-119$  and  $-196^\circ\text{C}$ . The lengthening of  $T_1$  is undoubtedly associated with the cessation of the hindered rotations of the  $\text{N}_2\text{H}_5$  groups. However,  $eQq/h$  showed no large changes between  $-196$  and  $-50^\circ\text{C}$  and the room temperature pattern for the irradiated and unirradiated samples were the same.

The experimental assistance of B. A. Jenkins is gratefully acknowledged.

<sup>33</sup> G. Burns, Bull. Am. Phys. Soc. 5, 159 (1960).

<sup>28</sup> P. Bailey, work is reported on p. 103 of reference 26.

<sup>29</sup> R. Bersohn, J. Chem. Phys. 29, 326 (1958).

<sup>30</sup> D. A. Anderson, Bull. Am. Phys. Soc. 6, 363 (1961) and private communication.

<sup>31</sup> T. G. Dunne and N. R. Stemple, Phys. Rev. 120, 1949 (1960), have found that the mixed system  $\text{Ba}(\text{Li,Al})_2(\text{F,O})_4$  is ferroelectric but the Li NMR was not measured since a sufficient amount of material could not be obtained.

<sup>32</sup> R. Pepinsky, K. Vedam, Y. Okaya, and S. Hoshino, Phys. Rev. 111, 1467 (1958).

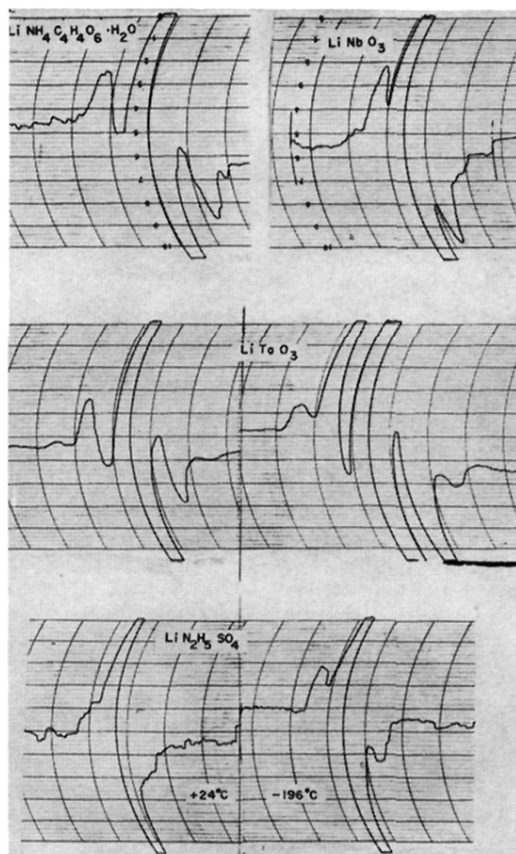


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