

only possible to say that the observed  $\delta g=0.12$  is not unreasonable since  $\lambda\sim 0.4$  eV is appropriate to indium  $5p$  states<sup>15</sup> and  $\Delta E\sim 4$  eV is the magnitude of the direct gap found in optical studies.<sup>5</sup>

The spin-lattice relaxation time due to ionized, substitutional impurity scattering at a single-valley band edge has also been discussed by Elliott<sup>14</sup> and Yafet.<sup>16</sup> The relation between  $T_1$  and  $\tau$  is expected to take the form

$$T_1\sim\tau/\delta g^2c^{2/3}, \quad (8)$$

where  $c$  is the fractional concentration of scattering centers. Taking  $c\sim 10^{-3}$  for  $\text{In}_2\text{O}_3$  we obtain  $T_1/\tau\sim 10^{-4}$ , which is at least three orders of magnitude smaller than is found experimentally. Yafet<sup>16</sup> has pointed out that for a single-valley extremum at a point of high symmetry in

<sup>15</sup> R. Braunstein and E. O. Kane, *J. Phys. Chem. Solids* **23**, 1423 (1962).

<sup>16</sup> Y. Yafet, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 14, p. 1.

momentum space and for impurity sites having inversion symmetry Eq. (8) should be multiplied by an additional factor of  $c^{-2/3}$ . While the symmetry requirements are not fulfilled in  $\text{In}_2\text{O}_3$  or the other II-VI compounds<sup>13</sup> such a factor would significantly reduce the discrepancy between theory and experiment. In view of the generality of the very large observed  $T_1/\tau$  ratios the problem of ionized impurity scattering for single-valley band edges deserves more careful theoretical examination.

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## $\text{Na}^{23}$ Quadrupole Interaction in Ferroelectric Rochelle Salt\*

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The first-order electric quadrupole splitting of the  $\text{Na}^{23}$  nuclear magnetic resonance has been studied in single crystals of undeuterated Rochelle salt. At 30°C, in the upper paraelectric phase, the quadrupole coupling constants and asymmetry parameters for all four  $\text{Na}^{23}$  sites were found to be the same:  $e^2Qq/h=1.313$  Mc/sec and  $\eta=0.809$ . At 0°C in the ferroelectric phase, two coupling constants were measured, corresponding to the lower crystal symmetry. The values are  $e^2Qq/h=1.285$  Mc/sec with  $\eta=0.872$ , and  $e^2Qq/h=1.407$  Mc/sec with  $\eta=0.675$ . These results were analyzed according to the model of Blinc, Petkovsek, and Zupanic in which the changes are due to displacements of one hydroxyl ion and one water molecule. The data fit the model well and lend support to their view of the structural changes that take place when Rochelle salt becomes ferroelectric.

### I. INTRODUCTION

THE macroscopic properties of Rochelle salt have been well known for a long time.<sup>1-4</sup> Rochelle salt ( $\text{NaK}$  tartrate tetrahydrate) has the unusual property that it is ferroelectric only between  $-18^\circ\text{C}$  and  $+24^\circ\text{C}$ . The structure is orthorhombic, with symmetry  $P2_12_12$

in both paraelectric phases.<sup>5</sup> The lattice undergoes a shear of  $1'48''$  in the  $bc$  plane,<sup>6</sup> becoming monoclinic in the ferroelectric phase with symmetry  $P2_1$  along  $a$ , the ferroelectric axis.<sup>7-9</sup> There are 4 molecules in the unit cell.

However, the structural problem has not been completed. The x-ray diffraction experiment of Beevers and Hughes was the first attempt to determine the structure

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<sup>1</sup> J. Hablutzel, *Helv. Phys. Acta* **12**, 489 (1939).

<sup>2</sup> H. Mueller, *Phys. Rev.* **47**, 175 (1935).

<sup>3</sup> W. Kanzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4.

<sup>4</sup> F. Jona and G. Shirane, *Ferroelectric Crystals* (The Macmillan Company, New York, 1962), Chap. VII.

<sup>5</sup> C. A. Beevers and W. Hughes, *Proc. Roy. Soc. (London)* **A177**, 251 (1941).

<sup>6</sup> A. R. Ubbelohde and I. Woodward, *Proc. Roy. Soc. (London)* **179**, 399 (1942).

<sup>7</sup> B. C. Frazer, M. McKeown, and R. Pepinsky, *Phys. Rev.* **94**, 1435 (1954).

<sup>8</sup> R. V. G. Sundra Rao, B. C. Frazer, and R. Pepinsky, in *Program and Abstract of the 11th Annual Conference on X-ray and Electron Diffraction*, Pittsburgh, 1953 (unpublished).

<sup>9</sup> F. Mazzi, F. Jona, and R. Pepinsky, *Bull. Am. Phys. Soc.* **1**, 131 (1956).

of Rochelle salt.<sup>5</sup> A reinvestigation of the structure was carried out by Krstanovic, Okaya, and Pepinsky using x-ray diffraction techniques which utilize high-speed computers.<sup>10</sup> The investigation found that in the ferroelectric state, the heavy atoms were not displaced from sites of orthorhombic symmetry. However, it was subsequently discovered that irradiation of Rochelle salt by x rays (or gamma rays) destroys ferroelectricity.<sup>11-14</sup> Under irradiation in the ferroelectric state, the atoms shift to locations of orthorhombic symmetry.<sup>15,16</sup>

A two-dimensional neutron-diffraction investigation has been carried out by Frazer *et al.* on deuterated Rochelle salt in the ferroelectric phase.<sup>8,9,16</sup> From this investigation, one ionic dipole has been definitely identified.<sup>16,17</sup> The hydrogen atom on (OH)<sub>5</sub>, in the notation of Beevers and Hughes,<sup>5</sup> is displaced from orthorhombic symmetry. Figure 1 shows the location of this dipole as well as the locations of the Na ions in the unit cell and the symmetry axes in the orthorhombic phase.

Further structural information can be obtained from a study of the Na<sup>23</sup> nuclear magnetic resonance (NMR) in Rochelle salt. This resonance is split by a nuclear quadrupole interaction and is therefore sensitive to the small atomic displacements that take place at the phase transitions. In addition, the sodium nucleus is quite close to the ionic dipole identified by Frazer. Therefore, a study of the first-order quadrupole splitting of the Na<sup>23</sup> NMR in Rochelle salt was undertaken and is reported here.

In an independent investigation Blinc, Petkovsek, and Zupancic<sup>18</sup> (hereafter referred to as BPZ) have studied the second-order shift of the central component of the Na<sup>23</sup> nuclear-magnetic-resonance spectrum in deuterated Rochelle salt. Their experiment ultimately yields the same information as the present experiment, but with a somewhat lower precision. Since the work presented here was carried out on undeuterated Rochelle salt, a comparison of the two results is quite informative and helps to complete the picture of the ferroelectric displacements in Rochelle salt.

This work can be divided into two parts. First, there is a study of Na<sup>23</sup> quadrupole coupling constants at 30°C and at 0°C. The measured differences are then interpreted in terms of atomic displacements and compared with the results of BPZ. Second, one Na<sup>23</sup> magnetic-resonance-satellite transition was studied continuously

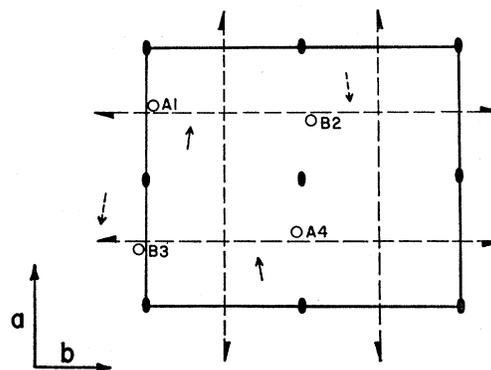


FIG. 1. A part of the  $ab$  plane of the unit cell of Rochelle salt. The open circles represent Na sites. Sites of the hydrogens of (OH)<sub>5</sub> are indicated by small arrows. Unit cell dimensions at 0°C are  $a = 11.867$  Å,  $b = 14.226$  Å, and  $c = 6.213$  Å.

as a function of temperature, particularly in the region near the upper transition point in order to determine the nature of the phase change.

## II. EXPERIMENTAL METHOD

The Na<sup>23</sup> NMR were observed with a Pound-Watkins-type radio-frequency spectrometer<sup>19</sup> and a Magnion-Harvey-Wells L-128 12-in. electromagnet. All frequency measurements were made with a Hewlett-Packard 524D electronic counter.

The Rochelle salt samples used in the experiments were all cut from a large single crystal purchased from Clevite, Inc. Each sample was cut in the shape of a cylinder 12 mm in diam and about 18 mm long. All crystals were cut with the axes along one of four crystal-line directions: parallel to either the  $a$ ,  $b$ , or  $c$  axis, or parallel to a line in the  $ac$  plane and making an angle of 45° with both the  $a$  and  $c$  axes.

The normal temperature of the laboratory in which this work was carried out was 30°C, so all measurements in the nonferroelectric state were made at room temperature. For measurements at lower temperatures the sample and coil were immersed in a Dewar flask of cooled iso-octane. This liquid was used because it has a low-dielectric constant and a high specific heat, and it does not interact with Rochelle salt.

In the high-temperature phase at 30°C, the satellites were first analyzed by a modified Volkoff method,<sup>20</sup> for crystal rotations about two axes that were not perpendicular to each other.<sup>21</sup> One of the two rotation axes used was parallel to the crystalline  $c$  axis, while the other was perpendicular to the  $b$  axis and bisected the angle between the  $a$  and  $c$  crystalline axes. Figure 2 is a plot of the measured splitting versus angle of rotation for the

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<sup>11</sup> K. Toyoda, A. Kawabota, and T. Tanaka, *Bull. Inst. Chem. Res. Kyoto Univ. (Japan)* **39**, 2, 189 (1961).

<sup>12</sup> K. Okada, *J. Phys. Soc. Japan* **16**, 414 (1961).

<sup>13</sup> G. C. Moulton and W. E. Moulton, *J. Chem. Phys.* **35**, 208 (1961).

<sup>14</sup> K. Okada, *J. Phys. Soc. Japan* **15**, 363 (1960).

<sup>15</sup> H. Boutin, B. C. Frazer, and F. Jona, *J. Phys. Chem. Solids* **24**, 1341 (1963).

<sup>16</sup> B. C. Frazer, *J. Phys. Soc. Japan, Suppl.* **17**, B-11 (1961).

<sup>17</sup> B. C. Frazer (private communication).

<sup>18</sup> R. Blinc, J. Petkovsek, and I. Zupancic, *Phys. Rev.* **136**, 1684 (1964).

<sup>19</sup> R. V. Pound and W. D. Knight, *Rev. Sci. Instr.* **21**, 219 (1950).

<sup>20</sup> G. M. Volkoff, H. E. Petch, and D. W. L. Smellie, *Can. J. Phys.* **30**, 270 (1952).

<sup>21</sup> M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 5.

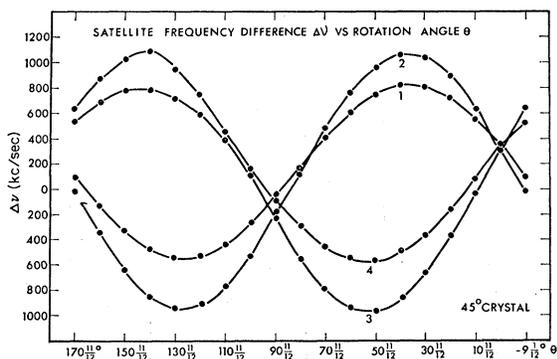


FIG. 2. Plot of  $\text{Na}^{23}$  satellite splitting versus angle of rotation for a rotation about an axis making an angle of  $45^\circ$  with both the  $a$  and  $c$  axes of Rochelle salt at  $30^\circ\text{C}$ . The four curves correspond to the four  $\text{Na}^{23}$  sites in the unit cell. The magnetic field strength was 10 370 G.

latter of the two rotation axes. The splittings shown on the graph were measured between pairs of satellite lines arising from  $\text{Na}^{23}$  nuclei in identical sites. This method subtracts out the second-order shifts of the satellites and makes possible a simple first-order analysis of the results.

However, the precision of this method is limited by the accuracy with which the crystals can be oriented, and by the precision with which the crystal rotation angles can be read. In this work the angles were read with a Keuffel and Esser protractor with  $\frac{1}{2}^\circ$  divisions which is attached to the apparatus. These limitations become quite significant in the present experiment where a difference in field gradient between two phases of the solid is to be measured.

To minimize the errors due to crystal orientation, the final measurements of the satellite splittings were made at a few selected crystal orientations at both  $30$  and  $0^\circ\text{C}$ . Thus the crystal was carefully oriented at  $30^\circ\text{C}$  and the satellite splittings were measured. Then, without moving the crystal, the system was cooled to  $0^\circ\text{C}$  and the changes in the splittings were measured. This procedure assured that the crystal orientation was the same at  $30$  and  $0^\circ\text{C}$ , and any change in the measured splitting was due to a change in the field gradient in the crystal. This entire procedure was carried out at each of the selected orientations.

Furthermore, the NMR spectrum in conjunction with the known crystal symmetries of Rochelle salt was used as much as possible to improve the precision with which the crystals could be oriented in these few selected positions.

Since there are 4 Na atoms per unit cell in Rochelle salt, in general 4 different pairs of satellite transitions can be expected. However, in the orthorhombic phase of this crystal there is either a twofold rotation axis or a twofold screw axis parallel to each crystal axis. These symmetry axes are indicated in Fig. 1. The symmetry operations associated with these axes interchange pairs of sodium atoms within the unit cell while leaving the overall crystal unchanged.

Thus, under one of the operations the  $\text{Na}^{23}$  NMR patterns due to these pairs of Na atoms are interchanged while leaving the total pattern unchanged. If one of these axes is perpendicular to the magnetic-field direction, then the twofold symmetry operation not only leaves the overall resonance pattern unchanged, but the pattern due to a single nucleus is also left unchanged. This means that the resonance patterns due to nuclei related by these symmetry operations are identical if a symmetry axis, i.e. a crystal axis, is perpendicular to the magnetic field. Thus, if one of the crystal axes is precisely oriented perpendicular to the magnetic-field direction the satellite lines superpose in pairs, and only two sets of satellites can be observed. Furthermore, if the magnetic field is parallel to a crystal axis, then the other two axes are perpendicular to the field, and all four sets of satellites become identical.

This satellite superposition technique proved to be the most accurate method available for positioning the crystals. Accordingly, all the orientations at which final readings were taken had at least one orthorhombic axis perpendicular to the magnetic field direction. The satellite splittings thus measured were interpreted according to the standard Volkoff equations.<sup>20</sup> These give, for the frequency difference between a pair of satellites, with the  $x$  axis perpendicular to the magnetic field direction,

$$\Delta\nu = A_x + B_x \cos 2\theta_x + C_x \sin 2\theta_x, \quad (1)$$

where

$$A_x = C(V_{yy} + V_{zz}) = -CV_{xx},$$

$$B_x = C(V_{yy} - V_{zz}),$$

$$C_x = 2CV_{yz},$$

and

$$C = \frac{eQ_{\text{Na}}}{2h}.$$

In these equations,  $\theta_x$  is the angle between the  $y$  axis and the magnetic-field direction. Similar expressions can be obtained for the cases of the  $y$  and  $z$  axes perpendicular to the magnetic field by permuting the indices. In these expressions  $eQ_{\text{Na}}$  is the  $\text{Na}^{23}$  nuclear quadrupole moment and the  $V_{ij}$  are the components of the electric-field-gradient tensor in the chosen coordinate system. For the work under discussion the orthorhombic crystal-line axes  $abc$  were chosen, respectively, as the  $xyz$  axes.

Since all 4 Na sites in the orthorhombic phase are related to each other by twofold rotations or twofold screw operations it follows that any one component of  $V_{ij}$  can differ from site to site only in sign. It also follows that any diagonal component  $V_{ii}$  is identical for all 4 sites in both magnitude and sign.

The final measurements were made for 7 different crystal orientations which served to over determine the 5 independent field-gradient components. The first three of these orientations had the magnetic field parallel, in turn, to each of the 3 orthorhombic crystal axes. Examination of Eq. (1) reveals that each of the satellite

TABLE I. Na<sup>23</sup> electric-field-gradient components (kc/sec) in crystal system of Rochelle salt. *A* and *B* are monoclinic sublattices at 0°C.

<i>T</i>	$2CV_{yz}$	$2CV_{xz}$	$2CV_{xy}$	$CV_{xx}$	$CV_{yy}$	$CV_{zz}$
30°C	215	78	1168	222	-164	-58
	±22	±8	±3	±½	±½	±½
0°C	264	33	1148	223	-175	-45½
<i>A</i>	±25	±10	±6	±1	±1	±1
0°C	195	100	1225	231	-125	-107
<i>B</i>	±25	±10	±6	±1	±1	±1

splittings measured at these orientations yields one of the diagonal components of the tensor  $CV_{ij}$ . Since these measurements were taken on the most precisely positioned crystals, the diagonal components of  $CV_{ij}$  were determined with greater accuracy than the off-diagonal components. The off-diagonal components were determined from the other 4 crystal orientations. These were: the *x* axis perpendicular to the magnetic-field direction with  $\theta_x=45^\circ$  and with  $\theta_x=135^\circ$ , the *y* axis perpendicular to the magnetic field direction and  $\theta_y=45^\circ$ , and the *z* axis perpendicular to the magnetic field and  $\theta_z=45^\circ$ .

Although these final measurements gave improved accuracy the initial rotation, experiments were necessary both to determine the relative signs of the components of  $CV_{ij}$ , and to aid in sorting the satellites into sets corresponding to different lattice sites. It was also necessary to take some measurements at intermediate angles at 0°C to aid in sorting the satellites that appeared in the ferroelectric phase.

### III. RESULTS

In the orthorhombic phase of Rochelle salt all four Na<sup>23</sup> sites give rise to the same quadrupole coupling constants since all 4 sites are related by the symmetry operations of the crystal. However, when the crystal is cooled and becomes monoclinic only the twofold screw axis parallel to the ferroelectric *a* axis remains. This lowered symmetry divides the Na<sup>23</sup> sites into 2 independent groups each of which possesses orthorhombic symmetry. Following the notation of BPZ these groups are labeled *A* and *B*. As a result of the orthorhombic symmetry of each group any component of the tensor  $CV_{ij}$  has the same magnitude for all nuclei within one group.

Table I gives the components of the tensor  $CV_{ij}$  in the crystal coordinate system. Only the magnitudes of the off-diagonal terms are given since these are the same for all Na<sup>23</sup> sites. The relative signs of the off-diagonal components are given in Table II for each of the four experimentally observed spectra. However, the signs of the diagonal components are given in Table I because these are unchanged from site to site.

An immediate consequence of the lowered symmetry of the monoclinic phase is that each satellite transition splits into two unless the ferroelectric *a* axis is perpen-

dicular to the magnetic-field direction. For orientations with the crystalline *b* or *c* axes perpendicular to the magnetic-field direction this splitting is due to the removal of the symmetry axes that caused the satellites to superpose in the orthorhombic phase.

However, for an arbitrary orientation with none of the crystalline axes perpendicular to the magnetic-field direction each satellite is still observed to split into two. At such an orientation, 4 pairs of satellites are observed in the orthorhombic phase, and these are doubled to 8 pairs in the monoclinic phase. These extra satellites are due to the crystal dividing into oppositely polarized domains. To verify that domains were the cause of the extra lines in the monoclinic phase, an electric field was applied parallel to the ferroelectric *a* axis. With the electric field in the positive *a* direction, half of the satellites disappeared while the other half doubled in intensity. When the direction of the electric field was reversed, the satellites that had disappeared returned at double their original intensity while the remaining satellites disappeared.

No evidence of domain structure appears if any one of the crystal axes is perpendicular to the magnetic field because oppositely polarized domains are twins of each other. One type domain is polarized along the positive *a* direction while its twin is polarized along the negative *a* direction. These twins go into each other under the two orthorhombic symmetry operations that were removed when the crystal became monoclinic. Thus the twinned domains present identical spectra with a crystal axis perpendicular to the magnetic-field direction.

The electric-field-gradient tensors given in Tables I and II were diagonalized to give the quadrupole-coupling constants and asymmetry parameters in both phases. These are shown in Table III together with the results of BPZ for deuterated Rochelle salt. The excellent agreement in the nonferroelectric state graphically demonstrates the absence of any Ubbelohde effect.<sup>22</sup> However, the differences in the ferroelectric state are to be expected since the spontaneous polarizations are very different for the two crystals.<sup>3</sup>

Table IV gives the direction cosines of the principal axes of the electric-field-gradient tensor for the Na<sup>23</sup> spectrum number one of Table I. The direction cosines for the other three tensors have the same magnitudes as these, differing only in sign, and their signs can be ob-

TABLE II. Relative signs of off-diagonal components of electric field gradient tensor.

	Na <sup>23</sup> Spectrum number				Notation of Miller and Casabella
	1	2	3	4	
$CV_{xy}$	+	+	-	-	
$CV_{xz}$	+	-	-	+	
$CV_{yz}$	+	-	+	-	
	1	3	4	2	Notation of BPZ

<sup>22</sup> A. R. Ubbelohde and I. Woodward, Proc. Roy. Soc. (London) 179, 399 (1942).

TABLE III. Na<sup>23</sup> Quadrupole coupling constant  $e^2Qq/h$  and asymmetry parameter  $\eta$  in Rochelle salt in the upper paraelectric and in the ferroelectric phases.

$T$	Undeuterated Rochelle salt		Deuterated Rochelle salt <sup>a</sup>	
	$e^2Qq/h$ (Mc/sec)	$\eta$	$e^2Qq/h$ (Mc/sec)	$\eta$
+30°C	1.313	0.809	1.313	0.800
0°C <i>A</i>	$\pm 0.014$	$\pm 0.021$	$\pm 0.015$	$\pm 0.03$
	1.285	0.872	1.323	0.803
0°C <i>B</i>	$\pm 0.0185$	$\pm 0.022$	$\pm 0.015$	$\pm 0.03$
	1.407	0.675	1.419	0.639
-40°C	$\pm 0.020$	$\pm 0.029$	$\pm 0.015$	$\pm 0.03$
			1.395	0.636
			$\pm 0.015$	$\pm 0.03$

<sup>a</sup> R. Blinc, J. Petkovsek, and I. Zupancic, Phys. Rev. **136**, 1684 (1964).

tained by applying the orthorhombic symmetry operations.

In addition to these studies at 30 and 0°C, a continuous study was made of one satellite in the temperature range from -40 to +40°C. This was done by cooling the entire system to the lower temperature and allowing it to warm up to room temperature, and then heating it slightly to 40°C. During this time the crystal was not moved, and one satellite line was monitored. The crystal used for this purpose had its axis of rotation at 45° to the *a* and *c* crystal axes. Figure 3 shows a plot of the frequency of the monitored satellite as a function of temperature.

The main purpose of this portion of the experiment was to obtain information about the changes that take place in the vicinity of the transition points. This technique was particularly well suited to studying the upper transition point. At that temperature the system was so close to ambient that it took several hours for the temperature of the crystal to change by 1 deg. Thus there was ample time to make precise measurements during the transition.

As Fig. 3 shows there were no discontinuous jumps in the satellite frequency at any temperature. Furthermore, the linewidth of the satellite did not change measurably in this experiment. To facilitate the linewidth measurements, the crystal used was oriented so that pairs of satellites never superposed. In addition, the particular crystal chosen for these measurements displayed a resonance pattern due to only one type of domain, indicating a crystal with a strong preferential polarization. Thus there were no problems due to overlapping resonances in measuring either the frequency or the linewidth of the satellite under scrutiny.

This rather unspectacular behavior of the satellite resonance demonstrates that the ferroelectric transition is not of first order. A first-order transition results in a discontinuity in the satellite frequency as observed in KNbO<sub>3</sub> by Cotts and Knight.<sup>23</sup> It also seems to rule out an order-disorder transition as in KH<sub>2</sub>PO<sub>4</sub>,<sup>4</sup> since such

<sup>23</sup> R. M. Cotts and W. D. Knight, Phys. Rev. **96**, 1285 (1954).

a transition would surely result in some measurable change in the linewidth of the Na<sup>23</sup> resonance.

#### IV. DISCUSSION

In the BPZ model the difference between the Na<sup>23</sup> electric field gradients on the *A* and *B* sublattices is due to a shift of one hydroxyl ion and one water molecule from positions of orthorhombic symmetry. The measured field-gradient differences can then be used to calculate the distances these units have shifted. The hydroxyl ion, (OH)<sub>5</sub>, is the same one identified by Frazer as a ferroelectric dipole.

The comparison of the results of the experiment described here with that of BPZ is facilitated if these results are put in the same form as theirs. Then the calculation of BPZ relating field-gradient changes to ion displacements can be used directly. The quantities to which BPZ finally relate the ion shifts are defined in terms of the quantities given in Table I as

$$\begin{aligned}
 2\Delta a_a &= 2[(CV_{xx})_B - (CV_{xx})_A], \\
 2\Delta a_b &= 2[(CV_{yy})_B - (CV_{yy})_A], \\
 2\Delta a_c &= 2[(CV_{zz})_B - (CV_{zz})_A], \\
 \Delta c_a &= 2[-(CV_{yz})_B - (CV_{yz})_A], \\
 \Delta c_b &= 2[-(CV_{zx})_B - (CV_{zx})_A], \\
 \Delta c_c &= 2[(CV_{xy})_B - (CV_{xy})_A],
 \end{aligned} \tag{2}$$

where all the quantities on the right are evaluated at 0°C.

To fit the model properly the differences on the right are to be taken between the Na<sup>23</sup> *B* site in the upper right of Fig. 1 and the *A* site in the upper left of the figure. In order to evaluate these terms it is necessary to deduce which of the four measured electric-field-gradient tensors is due to each of the 4 Na<sup>23</sup> sites. If any one of the tensors can be identified as being due to a particular nucleus, then the other 3 can be correctly assigned by employing the crystal symmetries. Thus there are only 4 possible choices. The assignment finally used was that one which best satisfied the internal checks of the BPZ model as described below. The

TABLE IV. For Na<sup>23</sup> electric-field gradient, direction cosines of principal axes (*XYZ*) relative to *xyz* crystal system. Average error is  $\pm 0.010$ . Na spectrum 1.

$T$	Crystal axis	Principal axis		
		<i>X</i>	<i>Y</i>	<i>Z</i>
30°C	<i>x</i>	0.178	0.574	0.799
	<i>y</i>	-0.021	-0.810	0.586
	<i>z</i>	-0.984	0.122	0.132
0°C <i>A</i>	<i>x</i>	0.208	0.559	0.803
	<i>y</i>	-0.068	-0.809	0.583
	<i>z</i>	-0.976	0.182	0.123
0°C <i>B</i>	<i>x</i>	0.157	0.592	0.791
	<i>y</i>	-0.008	-0.801	0.599
	<i>z</i>	-0.988	0.090	0.126

TABLE V. Change in Na<sup>23</sup> electric-field-gradient components (kc/sec)  $\Delta CV_{ij}$  from 30 to 0°C in Rochelle salt. Na<sup>23</sup> spectrum 1.

	$2\Delta CV_{yz}$	$2\Delta CV_{xz}$	$2\Delta CV_{xy}$	$\Delta CV_{xx}$	$\Delta CV_{yy}$	$\Delta CV_{zz}$
A	-49	45	20	+1	11	-12½
	±1	±3	±3	±½	±½	±½
B	20	-22	-57	-9	-39	49
	±2	±2	±4	±½	±½	±½
Angle at which measured and 135°	$\theta_x = 45^\circ$	$\theta_y = 45^\circ$	$\theta_z = 45^\circ$	$\theta_z = 0^\circ$	$\theta_z = 90^\circ$	$\theta_x = 90^\circ$

numbers beside the Na sites in Fig. 1 indicate the tensor finally assigned to each site. In addition each site is marked *A* or *B* to indicate to which subgroup it belongs. The *A* or *B* assignment is arbitrary since it is reversed in the oppositely polarized domain. Then the quantities in Eq. (2) are calculated by taking the differences between components of tensors *B2* and *A1* as indicated in Tables I and II.

These quantities could be calculated from the data in Tables I and II, but the results of this procedure would have very large errors. Instead it is better to go back to the experimental data. The satellite splittings were first measured at 30°C, and the change in these splittings was then measured when the crystal was cooled to 0°C. By using these measured changes it is possible to get accurate values for the quantities

$$\Delta CV_{ij} = (CV_{ij})_{30^\circ\text{C}} - (CV_{ij})_{0^\circ\text{C}}. \quad (3)$$

Each of these quantities is determined at a single crystal orientation without moving the crystal during the measurement. Table V gives the values of  $\Delta CV_{ij}$  together with the crystal orientation at which each was determined for spectrum No. 1. The magnitudes given in this table are correct for all 4 spectra, but the signs apply only to spectra No. 1. The signs of the other 3 spectra can be obtained by consulting Table II.

It is possible to calculate the quantities defined in Eq. (2) by using the  $\Delta CV_{ij}$  terms instead of the  $CV_{ij}$  terms, and thus reduce the error. When this is done properly the values of  $(CV_{ij})_{30^\circ\text{C}}$  can be made to sub-

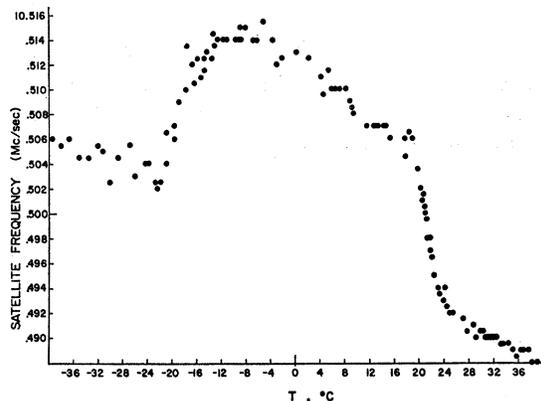


FIG. 3. Frequency of one Na<sup>23</sup> satellite as a function of temperature. The satellite used was the high-frequency satellite of spectrum number 3 in Fig. 2 at a magnetic field of 8844 G.

tract out of the expression giving the desired results. The expressions obtained in this manner for the *A1*, *B2* differences in terms of the  $\Delta C_{ij}$  quantities are given in Table VI together with the numerical results of using these expressions.

Only 5 of these quantities are independent since the sum of  $\Delta a_a$ ,  $\Delta a_b$ , and  $\Delta a_c$  must be zero. BPZ have chosen to use 4 of these values to calculate 4 ionic displacements and use the fifth value as a check on the model. The 4 displacements calculated are the *x*, *y*, and *z* displacements of H(5), the hydrogen on (OH)<sub>5</sub>, and the *x* displacement of O(8), the oxygen of (H<sub>2</sub>O)<sub>8</sub>, in the notation of Beevers and Hughes. The relationship between these displacements and the quantities in Table VI is expressed by the matrix equation<sup>24</sup>

$$\begin{bmatrix} 2\Delta a_a \\ 2\Delta a_b \\ \Delta c_a \\ \Delta c_c \end{bmatrix} = 0.33 \begin{bmatrix} 4.57 & 1.33 & 0.77 & 7.90 \\ 2.32 & 2.83 & -4.47 & 4.37 \\ 3.96 & -4.47 & -4.53 & 0.93 \\ 1.33 & 2.32 & 3.80 & 5.70 \end{bmatrix} \begin{bmatrix} \text{H}(5)\Delta X \\ \text{H}(5)\Delta Y \\ \text{H}(5)\Delta Z \\ \text{O}(8)\Delta X \end{bmatrix}. \quad (4)$$

In this matrix, which was calculated by BPZ for the Rochelle salt structure, the matrix elements have the units of 10<sup>5</sup> cps/Å. The auxiliary equation for  $\Delta c_b$  is

$$\Delta c_b = 0.77 \text{H}(5)\Delta X + 3.96 \text{H}(5)\Delta Y + 2.23 \text{H}(5)\Delta Z - 20.40 \text{O}(8)\Delta X. \quad (5)$$

Thus to be acceptable the ionic shifts obtained from Eq. (4) must give the correct value for  $\Delta c_b$  when substituted in Eq. (5). In addition to Eq. (5) the ion displacements obtained from Eq. (4) must also leave the distance between O(5) and H(5) unchanged according to the BPZ model. This condition together with Eq. (5) made it possible to decide on the correct association of Na<sup>23</sup> spectra with lattice positions. Only for the assignment used could both auxiliary conditions be satisfied to a reasonable degree.

The results of solving Eq. (4) for the ionic displacements are given in Table VII together with BPZ's results for deuterated Rochelle salt. If the displacements given in Table VII are substituted into Eq. (5),  $\Delta c_b$  is

TABLE VI. Difference between  $\Delta CV_{ij}$  for *A* and *B* monoclinic sublattices (kc/sec).

Notation of Miller and Casabella	Notation of BPZ	Calculated value (kc/sec)
$+2[\Delta(CV_{xx})_A - \Delta(CV_{xx})_B]$	$2\Delta a_a$	$20 \pm 2$
$+2[\Delta(CV_{yy})_A - \Delta(CV_{yy})_B]$	$2\Delta a_b$	$100 \pm 2$
$+2[\Delta(CV_{zz})_A - \Delta(CV_{zz})_B]$	$2\Delta a_c$	$-123 \pm 2$
$+2[+\Delta(CV_{yz})_A + \Delta(CV_{yz})_B]$	$\Delta c_a$	$-69 \pm 3$
$+2[+\Delta(CV_{xz})_A + \Delta(CV_{xz})_B]$	$\Delta c_b$	$67 \pm 5$
$+2[\Delta(CV_{xy})_A - \Delta(CV_{xy})_B]$	$\Delta c_c$	$77 \pm 7$

<sup>24</sup> R. Blinc (private communication). Three misprints occurred in the matrix, Eq. (23), which appeared in Ref. 22, but are corrected here. These misprints do not affect the calculated ion shifts.

TABLE VII. Calculated ionic displacements.

Displacements	Undeuterated Rochelle salt (Å)	Deuterated Rochelle salt <sup>a</sup> (Å)
$H_{(5)}\Delta X$	0.221	0.45
$H_{(5)}\Delta Y$	0.710	-0.01
$H_{(5)}\Delta Z$	-0.028	-0.25
$O_{(8)}\Delta X$	0.088	0.36
Error	$\pm 0.009$	$\pm 0.08$

<sup>a</sup> R. Blinc, J. Petkovsek, and I. Zupancic, Phys. Rev. 136, 1684 (1964).

calculated to be 37 kc/sec, while the experimental value given in Table VI is 67 kc/sec. The change in the O(5)-H(5) separation caused by the displacements of Table VII is found to be 0.1 Å. This agreement is adequate for the model used, but not as good as that obtained by BPZ for the deuterated salt.

Since the  $x$  direction is the direction of spontaneous polarization in Rochelle salt, the  $x$  displacements given in Table VII should be the main causes of that polarization. The measured value of the spontaneous polarization of undeuterated Rochelle salt at 0°C is well known to be lower than that of deuterated Rochelle salt at the same temperature. Therefore, the  $x$  displacements in Table VII are very encouraging because they are smaller in the undeuterated crystal than they are in the deuterated crystal.

A further check on the values in Table VII is obtained by calculating the spontaneous polarization due to the displacements listed there. The  $y$  and  $z$  displacements do not contribute to the polarization since there are two hydrogens per unit cell with displacements of the magnitudes given in Table VII. These are related by the twofold screw axis and thus their  $y$  and  $z$  displacements are in opposite directions. It is assumed that the charge on each hydrogen is positive and equal to 0.33 times the charge of the electron while the oxygen is negative and 0.66 times the electron charge; the same values used in calculating the matrix in Eq. (4). These values together with the displacements in Table VII lead to a spontaneous polarization of  $(1.6 \pm 0.5) \times 10^{-7}$  C/cm<sup>2</sup>. The measured polarization<sup>1</sup> at 0°C is  $2.5 \times 10^{-7}$  C/cm<sup>2</sup>.

Thus these displacements account for a large fraction of the total polarization which lends further support to the BPZ model. A similar calculation could be made for the deuterated crystal, but because of the larger experi-

mental errors due to the different experimental method employed, the error in the calculated polarization is too large to make the result meaningful.

It should be noted that, although the experimental results are more accurate for the undeuterated crystal, the results for the deuterated crystal better satisfied the auxiliary conditions imposed on the model. This is probably due to using Eq. (4), which was calculated for the deuterated crystal, in the undeuterated case. This was done because there is not enough structure data available to recalculate the matrix for the correct structure. Some of the matrix elements are very sensitive to the positions of ions in the unit cell, and small differences between the deuterated and undeuterated crystals, in the ferroelectric state, could easily explain the apparent discrepancy.

A further cause for concern is the large value of  $H_{(5)}\Delta y$  in the undeuterated crystal. Such a marked difference between the two crystals is quite surprising. It is possible that this displacement has been exaggerated by the use of Eq. (4) in the undeuterated salt, but in view of the way the model fits in other respects, it would be difficult to explain away the entire  $y$  displacement on this basis.

## V. CONCLUSION

The study of the first-order quadrupole splitting of the Na<sup>23</sup> nuclear magnetic resonance in undeuterated Rochelle salt lends support to the model of Blinc, Petkovsek, and Zupancic on 3 counts:

1. An analysis of the experimental data according to the model satisfies the internal checks of the model satisfactorily.

2. The ionic displacements in the direction of spontaneous polarization, calculated from the model, are smaller for the undeuterated salt than for the deuterated salt.

3. The spontaneous polarization due to the calculated ionic displacements is in reasonable agreement with the measured value of spontaneous polarization for the undeuterated salt.

In addition, the continuous study of one satellite resonance as a function of temperature indicates that the structure changes take place in a very smooth, gradual, orderly manner.